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Boundary conditions for electrochemical interfaces

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Abstract

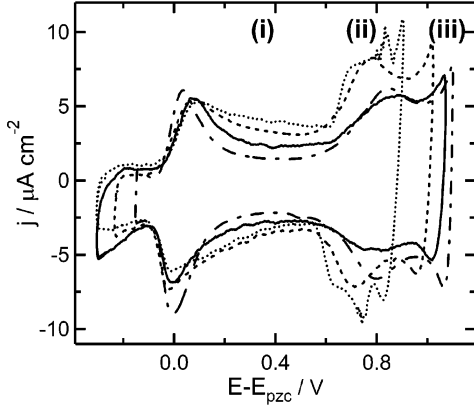
Consistent boundary conditions for electrochemical interfaces, which cover double layer charging, pseudo-capacitive effects and transfer reactions, are of high demand in electrochemistry and adjacent disciplines. Mathematical modeling and optimization of electrochemical systems is a strongly emerging approach to reduce cost and increase efficiency of super-capacitors, batteries, fuel cells, and electrocatalysis. However, many mathematical models which are used to describe such systems lack a real predictive value. Origin of this shortcoming is the usage of oversimplified boundary conditions. In this work we derive the boundary conditions for some general electrode-electrolyte interface based on non-equilibrium thermodynamics for volumes and surfaces. The resulting equations are widely applicable and cover also tangential transport. The general framework is then applied to a specific material model which allows the deduction of a current-voltage relation and thus a comparison to experimental data. Some simplified 1D examples show the range of applicability of the new approach.

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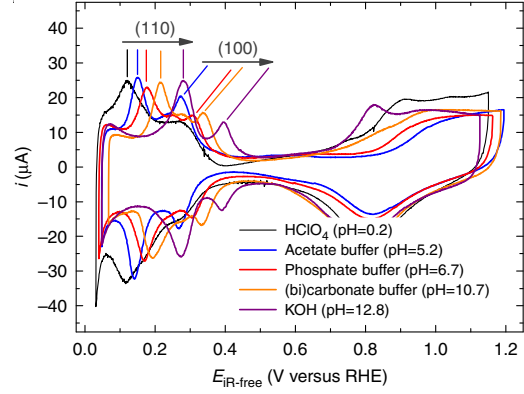
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(a) Cyclic voltammetry of UHV-prepared Ag(111) (dotted line), Ag(110) (solid line), and Ag(100) (dashed line) in 5 mM NaF + 1 mM NaOH. (Fig 4. of Ref [9])



(b) CVs of Pt(110) electrodes in contact with various aqueous electrolytes at a sweep rate of 50 mV/s (Fig. 3.a from Ref. [10])

Figure 1: Representative CVs for which no satisfactory theoretical model is available.

1 Introduction

Consistent boundary conditions for electrochemical interfaces are a key feature for a model based understanding of cyclic voltammetry, one of the main characterization methods in electrochemistry [1–5]. Even though many models exist to simulate cyclic voltammetry [6–8], but they lack some general fundament and have many shortcomings. In addition, a consistent coupling between the so called capacitive current charging the electrochemical double layer and the Faradaic current of some charge transfer reactions is yet outstanding. Up to date there is hence no model framework available which is able to predict complex CVs such as Fig. 1a and 1b.

This work uses the model framework of non-equilibrium thermodynamics and applies it in a general way to an electrode/electrolyte interface. The resulting boundary conditions can be applied to metal-electrolyte, liquid-liquid, intercalation electrode-electrolyte interfaces and many more.

2 Thermodynamic modeling

2.1 Domain and Species

We consider an electrolytic mixture Ω^E with species $A_\alpha, \alpha \in \mathcal{I}_E$, an electrode Ω^M with species $A_\alpha, \alpha \in \mathcal{I}_M$, and the electrode surface Σ with species/adsorbates $A_\alpha, \alpha \in \mathcal{I}_S$. The volume phases $\Omega^{E,M}$ are modeled with volumetric species densities $n_\alpha / \text{mol L}^{-1}$, where m_α denotes the molar mass and $e_0 z_\alpha$ the charge of the constituent A_α . The free charge density of each phase is denoted by $q_i = e_0 \sum_{\alpha \in \mathcal{I}_i} z_\alpha n_\alpha$ and the mass density

$\rho_i = \sum_{\alpha \in \mathcal{I}_i} m_\alpha n_\alpha$, $i = \text{E, M}$. We denote with

$$\mathcal{I}_{\text{EM}} = (\mathcal{I}_{\text{E}} \cup \mathcal{I}_{\text{M}}) . \quad (1)$$

the set of all electrolyte and electrode constituents.

The surface Σ is described in terms of surface densities $n_\alpha / \text{mol cm}^{-2}$ with charge number z_α of each adsorbate A_α , $\alpha \in \mathcal{I}_s$, and the surface charge density is $q = \sum_{\alpha \in \mathcal{I}_s} e_0 z_\alpha$. Note that there can be far more constituent present on the surface than in the volume phases. We denote thus with

$$\mathcal{I}_s^e = \mathcal{I}_s \setminus (\mathcal{I}_{\text{E}} \cup \mathcal{I}_{\text{M}}) \quad (2)$$

the species which are exclusively present on the surface.

The modeling procedure is based on the general framework of coupled non-equilibrium thermo-electrodynamics for volume and surface phases [11–14].

2.2 Chemical potentials

The chemical potentials of the constituent A_α , $\alpha \in \mathcal{I}_{\text{EM}}$ and A_α , $\alpha \in \mathcal{I}_s$ are derived based on some explicit free energy functions which describe the specific material. Within the theory of coupled volume and surface thermodynamics, independent free energy densities of the volume, i.e. $\rho\psi$, and the surface, ψ_s , arise. The derivation of these free energy functions is not scope of this work, and the detailed derivation is given in [15]. The chemical potentials of some constituent A_α in the volume and on the surface are given by

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial n_\alpha} \quad \text{and} \quad \mu_\alpha^s = \frac{\partial \psi_s}{\partial n_\alpha^s} . \quad (3)$$

Since we want to derive first rather general, material independent results in order to ensure applicability of the model for various electrochemical interfaces, e.g.

- metal/electrolyte,
- liquid/liquid
- metal/solid electrolyte,
- intercalation electrode/electrolyte,
- liquid metal/solid electrolyte,

we do not yet specify the explicit material functions of the phases Ω_{E} , Ω_{M} and Σ . Explicit examples are given in section 5.

2.3 Double layer

Adjacent to the surface Σ , two boundary or space charge layers Ω_M^{BL} and Ω_E^{BL} form [15], which build together with Σ the so called double layer [16]. This can be used to decompose the overall electrochemical interface in a handsome way.

We discuss briefly some aspects about coordinate transformations in the double layer regions which are necessary to proceed with the derivation. For $\mathbf{x} \in \Omega_i^{\text{BL}}$ and $\mathbf{x}_s \in \Sigma$ we have the representations

$$\mathbf{x} = x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z \quad \text{and} \quad \mathbf{x}_s = v\mathbf{b}_v + w\mathbf{b}_w = \mathbf{x}_s(v, w) \quad (4)$$

where \mathbf{e}_i are the cartesian coordinates and \mathbf{b}_i curvilinear covariant basis vectors of Σ . Consider now

$$\mathbf{x} = \mathbf{x}_s + u \cdot \mathbf{b}_u = \mathbf{x}(u, v, w) \quad (5)$$

with

$$\mathbf{b}_u = \frac{\mathbf{E}}{\langle \mathbf{E}, \mathbf{E} \rangle} . \quad (6)$$

This is actually the construction of a curvilinear coordinate system which follows the electric field lines. We have thus a parametrization of Ω_i^{BL} in terms of (u, v, w) with covariant basis vectors $(\mathbf{b}_u, \mathbf{b}_v, \mathbf{b}_w)$. Next, consider the curve

$$\gamma(u') = \mathbf{x}(u'; v, w) \quad u' \in [0, u] \quad (7)$$

for **fixed** values of (v, w) . Obviously this curve follows the electric field lines and we have

$$\frac{\partial}{\partial u} \gamma = \frac{\mathbf{E}}{\langle \mathbf{E}, \mathbf{E} \rangle} . \quad (8)$$

The electrostatic potential φ at some point $\mathbf{x} \in \Omega_i^{\text{BL}}$ can be traced back to $\mathbf{x}_s(v, w)$ on the surface along the curve γ , i.e.

$$\varphi(\mathbf{x}) - \varphi_s(v, w) = \int_{\gamma} \mathbf{E} \cdot d\mathbf{s} = \int_0^u \mathbf{E} \cdot \frac{\mathbf{E}}{\langle \mathbf{E}, \mathbf{E} \rangle} du' = \int_0^u 1 du' = u . \quad (9)$$

This shows that the third coordinate u of the curvilinear coordinate system (u, v, w) is actually the *potential distance* along γ to the surface potential. Note that electric field obeys with respect to the covariant basis the representations $\mathbf{E} = E_u \cdot \mathbf{b}_u$ and $\mathbf{E} = \nabla\varphi = (\partial_u\varphi)\mathbf{b}_u$, whereby $\|\mathbf{E}\| = |E_u|$. The arc-length of γ can be computed from

$$\text{len}(\gamma) = \int_{\gamma} 1 ds = \int_0^u \frac{1}{|E_u|} du' , \quad (10)$$

which shows that this approach only makes sense as long as the electric field does not vanish. Since within the space charge layer we have per definition $q_i \neq 0$, the Poisson equation $\text{div } \varepsilon_0(1 + \chi)\mathbf{E} = q_i$ states a non-vanishing electric field whereby this approach is valid.

Note that for a fixed value $u = U_i^{\text{BL}}$ equation (5) defines a hyper-surface Σ_i^{BL} *parallel* to Σ , i.e. $\mathbf{x}(U_i^{\text{BL}}; v, w) =: \mathbf{x}_s^{\text{BL}}(v, w)$. Per definition Σ and Σ_i^{BL} never intersect and are in some sense *parallel*, however, with respect to the potential distance and not necessary with respect to the distance along the normal vector of Σ .

If the surface potential is constant with respect to (v, w) , $\varphi(\mathbf{x}_s) = \varphi_s$ is actually a parametrization of Σ and thus

$$\frac{\nabla \varphi}{\|\nabla \varphi\|} \Big|_{\mathbf{x}_s} = \mathbf{n} \quad (11)$$

a normal vector of Σ . In this case Σ_i^{BL} is indeed a family of parallel surfaces. It is to emphasize that a special type of microscope actually uses this strategy to *map* a metal surface without touching it, i.e. the electrochemical force microscope [17].

This allows us to decompose the metal-electrolyte interface domain $\Omega = \Omega_{\text{M}} \cup \Sigma \cup \Omega_{\text{E}}$ into

$$\Omega = \Omega_{\text{M}} \cup \Sigma \cup \Omega_{\text{E}} = \Omega_{\text{M}}^* \cup \underbrace{\Omega_{\text{M}}^{\text{BL}} \cup \Sigma \cup \Omega_{\text{E}}^{\text{BL}}}_{=: \Sigma^{\text{DL}}} \cup \Omega_{\text{E}}^* , \quad (12)$$

where Ω_i^* are electro-neutral domains (i.e. $q_i = 0$). \mathbf{x}_i denote bulk points in each phase Ω_i^* , $i = \text{E}, \text{M}$, i.e. far away from the metal surface. An evaluation of n_α at the parallel-surface Σ_i^{BL} is frequently used and denoted by

$$n_\alpha \Big|_i^{\text{BL}} = n_\alpha \Big|_{\mathbf{x} \in \Sigma_i^{\text{BL}}} = n_\alpha \Big|_i^{\text{BL}}(v, w), \quad i = \text{E}, \text{M} , \quad (13)$$

where an evaluation at some bulk point \mathbf{x}_i far away from the the interface Σ^{DL} is denoted by $n_\alpha \Big|_{\mathbf{x}_i} = n_\alpha^i$, $i = \text{E}, \text{M}$.

2.4 Balance equations

Consider a species density $n_\alpha(\mathbf{x}, t)$, $\alpha \in \mathcal{I}_i$, $i = \text{E}, \text{M}$ which satisfies a balance equation

$$\frac{\partial n_\alpha}{\partial t} = -\text{div} (n_\alpha \mathbf{v} + \mathbf{J}_\alpha) + r_\alpha \quad \mathbf{x} \in \Omega_i, \quad (14)$$

where \mathbf{J}_α is the diffusional flux, \mathbf{v} the barycentric velocity and r_α the volumetric reaction rate of constituent A_α . This balance equation is subject to the boundary boundary condition (or surface balance)¹

$$\frac{\partial n_\alpha}{\partial t} = -\text{div}_s (n_\alpha \mathbf{w} + \mathbf{J}_\alpha) + 2k_M w_n n_\alpha \pm (\mathbf{J}_\alpha + n_\alpha (\mathbf{v} - \mathbf{w})) \cdot \mathbf{n} \Big|_\Sigma + r_\alpha , \quad (15)$$

¹Note that we assume here that a constituent A_α is either present in Ω_{M} , or in Ω_{E} , but not in both phases. Even though, e.g. a ion can be present in both phases, it is present in different states and thus distinguishable in terms of its species density, whereby we would have two balance equations.

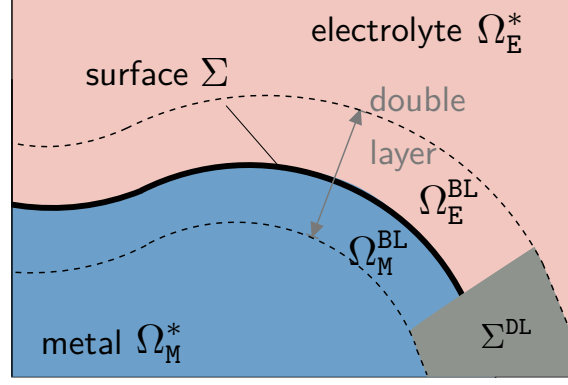


Figure 2: Sketch of the double layer forming at an interface between two charged domains Ω_M and Ω_E .

where $n_\alpha(\mathbf{x}_s, t)$ denotes the surface density, \mathbf{J}_α the tangential surface flux, div_s the surface divergence, r_α the surface reaction rate, k_M the mean curvature and w_n the normal velocity of the surface velocity \mathbf{w} . By convention, the $+$ sign in (15) holds for Ω_E and the $-$ sign for Ω_M .

The barycentric velocity \mathbf{v} and the surface velocity \mathbf{w} are determined from the respective momentum balances and we refer to [18] for detailed discussions. However, for the scope of this work we assume mechanical equilibrium [19]

$$\text{div}(\boldsymbol{\sigma}) = 0 \quad \text{and} \quad \llbracket \boldsymbol{\sigma} \rrbracket \mathbf{n} = -2k_M \gamma_s \mathbf{n} - \nabla_s \gamma_s \quad (16)$$

and a surface at rest, i.e. $\mathbf{w} = \mathbf{0}$. However, several aspects of the further derivation still hold for mechanical non-equilibrium by some careful re-derivation. $\boldsymbol{\sigma}$ denotes the total stress tensor and γ_s is the surface tension of the surface Σ . The double bracket denotes the jump at the interface. The total stress is given by

$$\boldsymbol{\sigma} = -(p\mathbf{Id} + \boldsymbol{\pi}) + (1 + \chi)\varepsilon_0 \left(\mathbf{E} \otimes \mathbf{E} - \frac{1}{2} \langle \mathbf{E}, \mathbf{E} \rangle \cdot \mathbf{Id} \right), \quad (17)$$

where the contribution of the electric field is called Maxwell stress [20] and $\boldsymbol{\pi}$ the viscous stress tensor. Viscous effects or more complex surface stress tensors can of course be included.

Note, however, that even in mechanical equilibrium \mathbf{v} is necessarily zero. But is not determined anymore from the momentum balance, as we shall see later. It is thus convenient for the further derivation to consider the balance equations in terms of the **net flux**

$$\mathbf{j}_\alpha = n_\alpha \mathbf{v} + \mathbf{J}_\alpha \quad \text{with} \quad \sum_{\alpha \in \mathcal{I}_i} \mathbf{j}_\alpha = n \mathbf{v} \quad i = E, M, \quad (18)$$

since we obtain the boundary conditions for these fluxes.

The decomposition of $\Omega_i = \Omega_i^* \cup \Omega_i^{BL}$ allows us to integrate (14) along the curve γ from $\mathbf{x}_s(v, w)$ to $\mathbf{x}_s^{BL}(v, w)$, i.e. to derive a surface balance equation from the thin boundary

layer part of the balance equation (14). This strategy was in detailed explained and derived by Grauel 1988 [21, 22], however, for parallel surfaces. But it applies straight forward to the constructed family of *potential-parallel surfaces* Σ_i^{BL} .

Following the derivation of Grauel we obtain

$$\frac{\partial n_\alpha^{\text{BL}}}{\partial t} = -\text{div}_s \mathbf{J}_\alpha^{\text{BL}} + r_\alpha^{\text{BL}} \quad (19)$$

$$\pm \mathbf{j}_\alpha \cdot \mathbf{n}|_i^{\text{BL}} \mp \mathbf{j}_\alpha \cdot \mathbf{n}|_\Sigma \quad (20)$$

for a thin boundary layer, with

$$n_\alpha^{\text{BL}} = \int_\gamma n_\alpha ds, \quad \mathbf{J}_\alpha^{\text{BL}} = \int_\gamma \mathbf{J}_\alpha^{\text{BL}} ds \quad \text{and} \quad r_\alpha^{\text{BL}} = \int_\gamma r_\alpha ds. \quad (21)$$

Combing (15) and (19) gives the double layer balance equation

$$\mp \mathbf{j}_\alpha \cdot \mathbf{n}|_i^{\text{BL}} = -\frac{\partial n_\alpha^{\text{DL}}}{\partial t} - \text{div}_s \mathbf{J}_\alpha^{\text{DL}} + r_\alpha^{\text{DL}} \quad (22)$$

with

$$n_\alpha^{\text{DL}} = n_\alpha^{\text{BL}} + n_\alpha, \quad \mathbf{J}_\alpha^{\text{DL}} = \mathbf{J}_\alpha + \mathbf{J}_\alpha^{\text{BL}} \quad \text{and} \quad r_\alpha^{\text{DL}} = r_\alpha^{\text{BL}} + r_\alpha \quad (23)$$

Note that (22) are actually the (flux) boundary condition at Σ^{DL} for the balance equation (14) in electro-neutral domains Ω_i^* , $i = \text{E, M}$. This is a crucial aspect, since we *shifted* the double layer contribution in the balance equations (14) into the **new boundary condition** (22). Equation (22) represent the most general type of boundary condition for an electro-neutral domain and covers all double layer charging effect as well as charge transfer reactions (i.e. Butler–Volmer-like expressions), as we see in the following sections.

Even though the definitions of n_α^{BL} and $\mathbf{J}_\alpha^{\text{BL}}$ seem to be inconvenient, it actually turns out that one is able to determine analytical expressions of the resulting integrals when the double layer is in equilibrium along the curve γ .

Note that the exclusive surface species $\alpha \in \mathcal{I}_s^e$ are subject to the surface balance equations

$$\frac{\partial n_\alpha}{\partial t} = -\text{div}_s \mathbf{J}_\alpha + r_\alpha \quad (24)$$

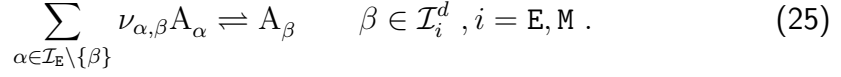
Summarizing, we consider thus volume balance equations in the two electro-neutral domains Ω_{E}^* and Ω_{M}^* and surface balance equations on the thin interface Σ^{DL} , which covers the electrolyte and metal boundary layers as well as the actual metal surface.

In order to proceed with the derivation, we have to specify the surface reactions occurring on the metal surface Σ .

2.5 Reactions

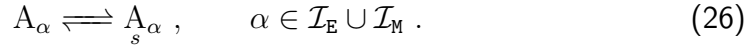
Goal of this section is to derive explicit representations of the surface reaction rates $r_{s\alpha}$ in the balance equations (22) and (24). We consider four general types of reactions:

- **Dissociation**, which occurs only within a single phase, *i.e.*

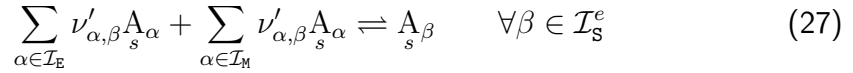


The reactions (25) define implicitly the species set \mathcal{I}_i^d of dissociative reaction products, *e.g.* $H^+ + OH^- \rightleftharpoons H_2O$ with $H_2O \in \mathcal{I}_E^d$.

- **Adsorption**, which is considered as the diffusion or jump process from a point $\mathbf{x} \rightarrow \mathbf{x}_s$ onto the the metal surface Σ , *i.e.*

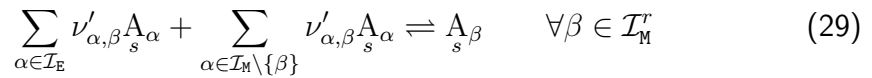
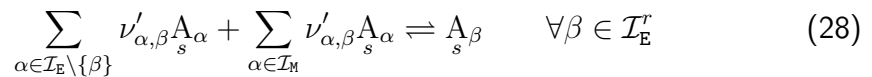


- **Surface reactions**, which are of general kind



Note that (27) serves actually to define implicitly the index set \mathcal{I}_s^e of the exclusive surface constituent. Consider, for example, the species H^+ in the electrolyte phase Ω_E and e^- in the electrode Ω_M . If atomic hydrogen H is not present in either of the bulk phases, but only on the surface as adsorbed H_s , we have the surface reaction $H_s^+ + e_s^- \rightleftharpoons H_s$ with $H_s \in \mathcal{I}_s^e$.

- **Transfer reactions**, which can be considered as surface reactions where the reaction product is present in either of the adjacent phases Ω_E^* or Ω_M^* . We can therefore write



Note that (28) and (29) actually serve to determine implicitly the subsets \mathcal{I}_E^r and \mathcal{I}_M^r of the reactive species, with $\mathcal{I}_{EM}^r = \mathcal{I}_E^r \cup \mathcal{I}_M^r$. For example, if we consider H_2 to be also a species present in the electrolyte phase as dissolved gas species, we have $2H_s^+ + 2e_s^- \rightleftharpoons H_{2s}$ as transfer reaction with $H_{2s} \in \mathcal{I}_E^r$.

3 Equilibrium assumptions and consequences

For the further derivation it is quite useful to simplify the model based on some plausible thermodynamic equilibrium assumptions.

3.1 Double layer in equilibrium

Throughout this work we assume that the space charge layers Ω_E^{BL} and Ω_M^{BL} adjacent to the metal surface Σ are in thermodynamic equilibrium along the arc γ . This assumption is justified by matched asymptotic methods [23] when the boundary layer is thin compared to the electro-neutral domains Ω_E^* and Ω_M^* . The equilibrium conditions read

$$\partial_u(\mu_\alpha + e_0 z_\alpha \varphi) \cdot \mathbf{b}_u = 0 \quad \alpha \in \mathcal{I}_i, \quad i = \text{E, M}. \quad (30)$$

Integration along the family of curves γ gives

$$\mu_\alpha \Big|_i^{\text{BL}} + e_0 z_\alpha U_i^{\text{BL}} = \mu_\alpha \Big|_{\mathbf{x} \in \Sigma_s} \quad \alpha \in \mathcal{I}_i, \quad i = \text{E, M} \quad (31)$$

with

$$U_i^{\text{BL}} = \varphi - \varphi \Big|_s^{\mathbf{x}_i^{\text{BL}}} \quad (v, w) \in S. \quad (32)$$

Note that this condition holds for every $(v, w) \in S$.

The equilibrium conditions (31) lead also to explicit representations of the boundary layer variables n_α^{BL} . Reconsider the definition of n_α^{BL} , i.e.

$$n_\alpha^{\text{BL}} = \int_\gamma n_\alpha ds. \quad (33)$$

Inserting the parametrization of γ gives

$$n_\alpha^{\text{BL}} = \int_0^{U_i^{\text{BL}}} n_\alpha \frac{1}{|E_u|} du. \quad (34)$$

It is to emphasize that the *units* of the integration in (34) is actually V. But due to the substitution of γ , the term $\frac{1}{|E_u|}$ arises with units m V^{-1} , which thus gives indeed units of mol m^{-2} for n_α^{BL} . Hence, in order to *perform* actually the integration of (34), we seek expressions

$$n_\alpha = \hat{n}_\alpha(u) \quad \text{and} \quad E_u = \hat{E}_u(u), \quad (35)$$

where u is the coordinate of the curvilinear base vector \mathbf{b}_u . This the real importance of the substitution in (34) and the introduction of the curvilinear coordinate system in the space charge layer. Surprisingly, it is indeed possible to find such representations for some explicit material functions of μ_α . We provide representations of representative materials (incompressible liquid electrolyte, metal electrode, intercalation electrode) in section 5.1 and proceed meanwhile with the general representation $n_\alpha^{\text{BL}} = \hat{n}_\alpha^{\text{BL}}(U_i^{\text{BL}})$, $\alpha \in \mathcal{I}_i$, $i = \text{E, M}$.

3.2 Reactions

3.2.1 Dissociation

The dissociation reactions (25) are assumed to be in equilibrium throughout this work. This entails the equilibrium condition

$$\sum_{\alpha \in \mathcal{I}_E \setminus \{\beta\}} \nu_{\alpha,\beta} \mu_\alpha = \mu_\beta, \quad (36)$$

for the index set \mathcal{I}_i^d of the dissociation reaction products in Ω_i , $i = E, M$. Note that this does not necessarily entail complete dissociation but rather computes the concentration of some constituent, e.g. the H^+ and OH^- concentration (or pH-value) due to the auto-protolytic reaction $H^+ + OH^- \rightleftharpoons H_2O$.

3.2.2 Adsorption

Throughout this work we assume that the adsorption process is always in equilibrium, which entails the condition

$$\mu_\alpha \Big|_{\mathbf{x} \in \Sigma} = \mu_\alpha \Big|_s, \quad \alpha \in \mathcal{I}_E \cup \mathcal{I}_M. \quad (37)$$

However, since we assume that the boundary layers are also in equilibrium, we can *trace back* the chemical potential μ_α at Σ along the curve γ to the the point \mathbf{x}_s^{BL} and obtain

$$\mu_\alpha \Big|_i^{\text{BL}} + e_0 z_\alpha U_i^{\text{BL}} = \mu_\alpha \Big|_s \quad (v, w) \in S. \quad (38)$$

This describes actually the superposition of adsorption and diffusion through the boundary layer. In order to emphasize this we employ the typeface

$$A_\alpha \Big|_i^{\text{BL}} \rightleftharpoons A_\alpha \Big|_s, \quad \alpha \in \mathcal{I}_i, i = E, M, \quad (39)$$

for this process.

Quite similar to the boundary layer it is possible to obtain explicit representations of n_α in terms of U_i^{BL} based on material functions of μ_α . Explicit representations are given in section 5.1 and we proceed the discussion with the general representation $n_\alpha = \hat{n}_\alpha(U_i^{\text{BL}})$, $\alpha \in \mathcal{I}_i$, $i = E, M$.

3.2.3 Surface reactions

Since we assume that the diffusion of the constituents A_α , $\alpha \in \mathcal{I}_i$, $i = E, M$ through the corresponding boundary layers and the subsequent adsorption are in equilibrium, we can rewrite (27) as

$$\sum_{\alpha \in \mathcal{I}_E} \nu_{\alpha,\beta} A_\alpha \Big|_E^{\text{BL}} + \sum_{\alpha \in \mathcal{I}_M} \nu_{\alpha,\beta} A_\alpha \Big|_M^{\text{BL}} \rightleftharpoons A_\beta \Big|_s \quad \forall \beta \in \mathcal{I}_S^e, \quad (40)$$

where the typeface $A_\alpha|_E^{\text{BL}}$ and $A_\alpha|_M^{\text{BL}}$ emphasizes this aspect. The reaction rate of this net reaction is denoted by R_β^S . Possible reactions are, for example, adsorption with subsequent de-solvation or partial charge transfer [15, 24].

We assume that all net surface reactions which can be written as (40) are in thermodynamic equilibrium, which provides the condition

$$\sum_{\alpha \in \mathcal{I}_E} \nu_{\alpha,\beta} (\mu_\alpha|_E^{\text{BL}} + e_0 z_\alpha U_E^{\text{BL}}) + \sum_{\alpha \in \mathcal{I}_M} \nu_{\alpha,\beta} (\mu_\alpha|_M^{\text{BL}} + e_0 z_\alpha U_M^{\text{BL}}) = \mu_\beta \quad \beta \in \mathcal{I}_S^e. \quad (41)$$

Note that the charge number of A_β is

$$\sum_{\alpha \in \mathcal{I}_E} \nu_{\alpha,\beta} z_\alpha + \sum_{\alpha \in \mathcal{I}_M} \nu_{\alpha,\beta} z_\alpha = z_\beta \quad (42)$$

in order to ensure the electroneutrality condition of the reaction (27).

For the adsorbates A_β we provide explicit material functions μ_β in section B which lead to representation $n_\beta = \hat{n}_\beta(U_E^{\text{BL}}, U_M^{\text{BL}})$, $\beta \in \mathcal{I}_S^e$.

3.2.4 Transfer reactions

The equilibrium condition of diffusion through the double layer, adsorption and subsequent surface reactions allows us to rewrite the general transfer reactions (28) and (29) as net reactions

$$\sum_{\alpha \in \mathcal{I}_{EM} \setminus \{\beta\}} \nu_{\alpha,\beta} A_\alpha|_E^{\text{BL}} \rightleftharpoons A_\beta|_E^{\text{BL}} \quad \beta \in \mathcal{I}_{EM}^r, \quad (43)$$

with reaction rate R_β^T and index set $\mathcal{I}_{EM}^r \cup \mathcal{I}_M^r$ of all reactive species. Possible examples of transfer reactions are

- $2 \text{H}^+|_E + 2 \text{e}^-|_M \rightleftharpoons \text{H}_2|_E$ (*hydrogen evolution*)
- $\text{Cu}^+|_M - \text{e}^-|_M \rightleftharpoons \text{Cu}_2^+|_E$ (*metal deposition/dissolution*)
- $\text{Na}^+|_E \rightleftharpoons \text{Na}^+|_M$ (*dissolution in Hg*)
- $\text{Fe}_3^+|_E + \text{e}^-|_M \rightleftharpoons \text{Fe}_2^+|_E$ (*Redox shuttle*)
- $\text{Li}^+|_E + \text{e}^-|_M \rightleftharpoons \text{Li}|_M$ (*intercalation*).

The metal and electrolyte species which are **not** a reaction product of a transfer reaction are denoted by

$$\mathcal{I}'_E = \mathcal{I}_E \setminus \mathcal{I}_E^r \quad \text{and} \quad \mathcal{I}'_M = \mathcal{I}_M \setminus \mathcal{I}_M^r, \quad \text{with} \quad \mathcal{I}'_{EM} = \mathcal{I}'_E \cup \mathcal{I}'_M. \quad (44)$$

For the charge numbers of the involved constituents we have the condition

$$\sum_{\alpha \in \mathcal{I}_{\text{EM}} \setminus \beta} \nu_{\alpha, \beta} z_{\alpha} = z_{\beta} \quad \beta \in \mathcal{I}_{\text{EM}}^r. \quad (45)$$

Transfer reactions are **not** assumed to be in equilibrium throughout this work. The equilibrium condition of (43) (for $\beta \in \mathcal{I}_i^r, i = \text{E}, \text{M}$)

$$\sum_{\alpha \in \mathcal{I}_{\text{E}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{E}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{E}}^{\text{BL}}) + \sum_{\alpha \in \mathcal{I}_{\text{M}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{M}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{M}}^{\text{BL}}) \stackrel{!}{=} \mu_{\beta}|_i^{\text{BL}} + e_0 z_{\alpha} U_i^{\text{BL}}, \quad (46)$$

would imply constant values of U_{E}^{BL} and U_{M}^{BL} . Since we seek to vary the potential U_{E}^{BL} (i.e. potentiometry), as we show in the next sections, this is untenable.

However, surface thermodynamics dictates that the reaction rates R_{β}^T of the transfer reactions (43) are related to (46) [25] via (for $\beta \in \mathcal{I}_i^r, i = \text{E}, \text{M}$)

$$R_{\beta}^T = L_{\beta}^T \cdot \left(e^{\frac{\alpha_{\beta}}{k_{\text{B}} T}} \left(\sum_{\alpha \in \mathcal{I}_{\text{E}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{E}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{E}}^{\text{BL}}) + \sum_{\alpha \in \mathcal{I}_{\text{M}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{M}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{M}}^{\text{BL}}) - \mu_{\beta}|_i^{\text{BL}} - e_0 z_{\alpha} U_i^{\text{BL}} \right) \right. \\ \left. - e^{-\frac{(1-\alpha_{\beta})}{k_{\text{B}} T}} \left(\sum_{\alpha \in \mathcal{I}_{\text{E}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{E}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{E}}^{\text{BL}}) + \sum_{\alpha \in \mathcal{I}_{\text{M}}} \nu_{\alpha, \beta} (\mu_{\alpha}|_{\text{M}}^{\text{BL}} + e_0 z_{\alpha} U_{\text{M}}^{\text{BL}}) - \mu_{\beta}|_i^{\text{BL}} - e_0 z_{\alpha} U_i^{\text{BL}} \right) \right) \quad (47)$$

with $L_{\beta}^T \geq 0$ for $\beta \in \mathcal{I}_{\text{EM}}^r$. This is the most general form of a thermodynamically consistent expression for a transfer reaction rate.

3.3 Boundary conditions

Base on the reaction rates of (40) and (43), the surface production rates r_{α} obey a specific structure, i.e.

$$r_{\alpha} = \begin{cases} -\sum_{\beta \in \mathcal{I}_{\text{S}}^e} \nu_{\beta, \alpha} R_{\beta}^S - \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta, \alpha} R_{\beta}^T, & \text{if } \alpha \in \mathcal{I}_{\text{EM}}' \\ -\sum_{\beta \in \mathcal{I}_{\text{S}}^e} \nu_{\beta, \alpha} R_{\beta}^S + R_{\alpha}^T - \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta, \alpha} R_{\beta}^T, & \text{if } \alpha \in \mathcal{I}_{\text{EM}}^r \\ R_{\alpha}^S, & \text{if } \alpha \in \mathcal{I}_{\text{S}}^e \end{cases} \quad (48)$$

Reinsertion of the production rates in (22) and some calculations lead to the boundary conditions ($\alpha \in \mathcal{I}_i, i = \text{E}, \text{M}$)

$$\pm \mathbf{j}_{\alpha} \cdot \mathbf{n}|_i^{\text{BL}} = \frac{\partial n_{\alpha}^{\text{Eff}}}{\partial t} + \text{div}_{\text{S}} \mathbf{J}_{\alpha}^{\text{Eff}} - r_{\alpha}^{\text{Eff}} \quad (49)$$

with

$$n_{\alpha}^{\text{Eff}} = n_{\alpha}^{\text{DL}} + \sum_{\beta \in \mathcal{I}_s^e} \nu_{\beta, \alpha} n_{\beta} \quad (50)$$

$$\mathbf{J}_{\alpha}^{\text{Eff}} = \mathbf{J}_{\alpha}^{\text{DL}} + \sum_{\beta \in \mathcal{I}_s^e} \nu_{\beta, \alpha} \mathbf{J}_{\beta} \quad (51)$$

$$r_{\alpha}^{\text{Eff}} = \begin{cases} r_{\alpha}^{\text{DL}} - \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta, \alpha} R_{\beta}^T, & \text{if } \alpha \in \mathcal{I}_{\text{EM}}' \\ r_{\alpha}^{\text{DL}} + R_{\alpha}^T - \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta, \alpha} R_{\beta}^T, & \text{if } \alpha \in \mathcal{I}_{\text{EM}}^r \end{cases} \quad (52)$$

The abbreviation $^{\text{Eff}}$ emphasizes that only the effective linear combinations (50)-(52) arise in the boundary conditions (49).

Note that the (equilibrium) representations of $\hat{n}_{\alpha}^{\text{BL}}(U_i^{\text{BL}})$, $\hat{n}_{\alpha}(U_i^{\text{BL}})$, $\alpha \in \mathcal{I}_{\text{EM}}$ and $\hat{n}_{\beta}(U_{\text{E}}^{\text{BL}}, U_{\text{M}}^{\text{BL}})$, $\beta \in \mathcal{I}_s^e$ lead to the representations ($\alpha \in \mathcal{I}_i$, $i, j = \text{E, M}$, $i \neq j$)

$$\pm \mathbf{j}_{\alpha} \cdot \mathbf{n}_i^{\text{BL}} = C_{\alpha}^{\text{Eff}} \cdot \frac{dU_i^{\text{BL}}}{dt} + C_{\alpha}^{\text{Pseu}, j} \cdot \frac{dU_j^{\text{BL}}}{dt} + \text{div}_s \mathbf{J}_{\alpha}^{\text{Eff}} - r_{\alpha}^{\text{Eff}} \quad (53)$$

with

$$C_{\alpha}^{\text{Eff}} = C_{\alpha}^{\text{BL}} + C_{\alpha} + C_{\alpha}^{\text{Pseu}, i} \quad \alpha \in \mathcal{I}_i, \quad i = \text{E, M} \quad (54)$$

$$C_{\alpha}^{\text{BL}} = \frac{dn_{\alpha}^{\text{BL}}}{dU_i^{\text{BL}}}, \quad C_{\alpha} = \frac{dn_{\alpha}}{dU_i^{\text{BL}}} \quad \alpha \in \mathcal{I}_i, \quad i = \text{E, M} \quad (55)$$

$$\text{and } C_{\alpha}^{\text{Pseu}, j} := \frac{d}{dU_j^{\text{BL}}} \left(\sum_{\beta \in \mathcal{I}_s^e} \nu_{\beta, \alpha} n_{\beta} \right) \quad \alpha \in \mathcal{I}_i, \quad i, j = \text{E, M}. \quad (56)$$

This are the most general boundary conditions for an electrochemical interface, including double layer charging, pseudo-capacity effect, transfer reactions, tangential surface diffusion, curvature effects.

The equations (131) are then the actual boundary conditions for the balance equations (14) in the electro-neutral domains Ω_i^* (i.e. with $q_i = 0$ in Ω_i , $i = \text{E, M}$). These boundary conditions hold for each charged interface, however, are not solvable yet since the number of unknowns is not equal to the number actual balance equations. In order to obtain a closed equation system, we require explicit representations of C_{α}^{Eff} , C_{α}^{Pseu} , and r_{α}^{Eff} , which requires specified material functions μ_{α} and $\mu_{\alpha, s}$.

4 Current/Voltage relation

4.1 Measured Current

The electrode Ω_{M}^* with boundary $\partial\Omega_{\text{M}} = \Sigma_{\text{M}}^* \cup \Sigma_{\text{M}}^{\text{inert}} \cup \Sigma_{\text{M}}^{\text{BL}}$ is connected via the surface Σ_{M}^* to an ampere-meter. Hence, the measured current I / A corresponds to the flux of

charge through Σ_M^* , i.e.

$$I = - \int_{\Sigma_M^*} \mathbf{j}_{q_M} \cdot d\mathbf{A}. \quad (57)$$

We assume that no current flows through the *inert* part of the electrode boundary, i.e. $\mathbf{j}_{q_M} = 0$ on Σ_M^{inert} . The global balance of q_M reads

$$\frac{d}{dt} \int_{\Omega_M^*} q_M dV = I + \int_{\Sigma_M^{\text{BL}}} \mathbf{j}_{q_M} \cdot d\mathbf{A}. \quad (58)$$

Since $q_M = 0$ in Ω_M^* , we obtain with eq. (49)

$$I = \int_{\Sigma_{\text{DL}}} \frac{\partial}{\partial t} (q_M^{\text{DL}} + q_M^{\text{Pseu}}) - r_{q_M}^{\text{Eff}} dA, \quad (59)$$

where

$$q_M^{\text{DL}} = e_0 \sum_{\alpha \in \mathcal{I}_M} z_\alpha n_\alpha^{\text{DL}}, \quad (60)$$

$$q_M^{\text{Pseu}} = e_0 \sum_{\alpha \in \mathcal{I}_M} z_\alpha \sum_{\beta \in \mathcal{I}_s^e} \nu_{\beta, \alpha} n_\beta, \quad (61)$$

$$r_{q_M}^{\text{Eff}} = e_0 \sum_{\alpha \in \mathcal{I}_M} z_\alpha r_\alpha^{\text{Eff}}. \quad (62)$$

The electroneutrality condition of the whole double layer states

$$q_M^{\text{DL}} + q_E^{\text{DL}} + q_s^e = 0 \quad \text{with} \quad q_s^e = e_0 \sum_{\alpha \in \mathcal{I}_s^e} z_\alpha n_\alpha \quad (63)$$

and leads to

$$I = \int_{\Sigma_{\text{DL}}} \frac{\partial}{\partial t} (q_E^{\text{DL}} + q_s^e - q_M^{\text{Pseu}}) - r_{q_M}^{\text{Eff}} dA \quad (64)$$

Note that with eq. (42) we have

$$q_s^e - q_M^{\text{Pseu}} = e_0 \sum_{\alpha \in \mathcal{I}_s^e} \left(z_\alpha - \sum_{\beta \in \mathcal{I}_M} z_\beta \nu_{\alpha, \beta} \right) n_\alpha = e_0 \sum_{\alpha \in \mathcal{I}_s^e} \left(\sum_{\beta \in \mathcal{I}_E} z_\beta \nu_{\alpha, \beta} \right) n_\alpha = \quad (65)$$

in order to ensure the electroneutrality of the surface reactions. The quantity

$$\sum_{\beta \in \mathcal{I}_E} z_\beta \nu_{\alpha, \beta} = z_\alpha^E, \quad \text{for } \alpha \in \mathcal{I}_s^e, \quad (66)$$

can be considered as the *pseudo*-charge of the adsorbates A_α , $\alpha \in \mathcal{I}_s^e$, since the constituents incorporated in

$$q_E^{\text{Pseu}} = e_0 \sum_{\alpha \in \mathcal{I}_s^e} z_\alpha^E n_\alpha \quad (67)$$

are not necessarily charged. The quantity

$$q_E^{\text{Eff}} := q_E^{\text{DL}} + q_E^{\text{Pseu}} \quad (68)$$

is then the effective electrolytic charge in the double layer and the measurable current writes as

$$I = \int_{\Sigma_{\text{DL}}} \frac{\partial}{\partial t} q_E^{\text{Eff}} - r_{q_M}^{\text{Eff}} dA . \quad (69)$$

Due to the equilibrium representations $\hat{n}_\alpha^{\text{DL}}(U_E^{\text{BL}})$, $\alpha \in \mathcal{I}_E$ and $\hat{n}_s^{\text{BL}}(U_E^{\text{BL}}, U_M^{\text{BL}})$, $\beta \in \mathcal{I}_S^e$ (c.f. section 3), the effective double layer charge q_E^{Eff} has a representation

$$q_E^{\text{Eff}}(U_E^{\text{BL}}, U_M^{\text{BL}}) = q_E^{\text{DL}}(U_E^{\text{BL}}) + q_E^{\text{Pseu}}(U_E^{\text{BL}}, U_M^{\text{BL}}) . \quad (70)$$

Hence we obtain

$$I = \int_{\Sigma_{\text{DL}}} \left(C_E^{\text{Eff}}(U_E^{\text{BL}}; v, w) \cdot \frac{dU_E^{\text{BL}}}{dt} + C_E^{\text{Pseu}, M}(U_E^{\text{BL}}, U_M^{\text{BL}}; v, w) \cdot \frac{dU_M^{\text{BL}}}{dt} - r_{q_M}^{\text{Eff}} \right) dA . \quad (71)$$

with

$$C_E^{\text{Eff}} = \frac{dq_E^{\text{Eff}}}{dU_E^{\text{BL}}} \quad \text{and} \quad C_E^{\text{Pseu}, M} = \frac{dq_E^{\text{Pseu}}}{dU_M^{\text{BL}}} . \quad (72)$$

C_E^{Eff} is then the effective differential capacity of the interface and $C_{E, M}^{\text{Pseu}}$ the metallic *pseudo*-capacity. Note that due to the decomposition $q_E^{\text{Eff}} = q_E^{\text{BL}} + q_s^{\text{BL}} + q_E^{\text{Pseu}}$ the differential capacity C_E^{Eff} decomposes into

$$C_E^{\text{Eff}} = C_E^{\text{BL}} + C_s + C_E^{\text{Pseu}, E} \quad (73)$$

with boundary layer capacity $C_E^{\text{BL}} = \frac{dq_E^{\text{BL}}}{dU_E^{\text{BL}}}$, surface capacity $C_s = \frac{dq_s}{dU_E^{\text{BL}}}$, and electrolytic *pseudo*-capacity $C_E^{\text{Pseu}, E} = \frac{dq_E^{\text{Pseu}}}{dU_E^{\text{BL}}}$.

However, C_E^{Pseu} and $C_{E, M}^{\text{Pseu}}$ are inherently different since $C_{E, M}^{\text{Pseu}}$ vanishes when $U_M^{\text{BL}} = \text{const.}$, which is for example the case for an ideal metal.

Next we discuss the reaction rate $r_{q_M}^{\text{Eff}}$. Note that the term $\sum_{\alpha \in \mathcal{I}_M} z_\alpha r_\alpha^{\text{DL}}$ vanishes due to the electroneutrality condition of the dissociation reactions. Reinsertion of the definition (52) and using eq. (45) gives, with

$$z_\beta^M := \sum_{\alpha \in \mathcal{I}_M} \nu_{\alpha, \beta} z_\alpha , \quad \beta \in \mathcal{I}_E^r \quad \text{and} \quad z_\beta^E := \sum_{\alpha \in \mathcal{I}_E} \nu_{\alpha, \beta} z_\alpha , \quad \beta \in \mathcal{I}_M^r , \quad (74)$$

after some calculation (see appendix B)

$$r_{q_M}^{\text{Eff}} = e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_\alpha^E R_\alpha^T - e_0 \sum_{\alpha \in \mathcal{I}_E^r} z_\alpha^M R_\alpha^T . \quad (75)$$

The transfer reaction rates R_α^T are given in eq. (47) with $R_\alpha^T = \hat{R}_\alpha^T(U_E^{\text{BL}}, U_M^{\text{BL}})$.

Since most experimental setups the current is *normalized* to the surface area A_Σ of the electrode, we obtain the final expression of the measurable current density

$$i = \frac{1}{A_\Sigma} \int_{\Sigma_{\text{DL}}} \left(C_E^{\text{Eff}} \cdot \frac{dU_E^{\text{BL}}}{dt} + C_{E,M}^{\text{Pseu}} \cdot \frac{dU_M^{\text{BL}}}{dt} - e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_\alpha^E R_\alpha^T + e_0 \sum_{\alpha \in \mathcal{I}_E^r} z_\alpha^M R_\alpha^T \right) dA . \quad (76)$$

Note that this relation is the actual measuring instruction for any comparison of a continuum model to experimental data. It is the most general expression for a single surface phase and covers adsorption effects, surface reactions and pseudo-capacitance, as well as transfer reactions. In general it is the *a posteriori* relation to compute the current for given (numerical) solutions of the state variables of the interface.

4.2 Measured potential

Yet we have introduced the boundary layer potential drops U_E^{BL} and U_M^{BL} of a single electrochemical interface. However, there can arise additional potential drops in the electro-neutral domains Ω_E^* and Ω_M^* , namely

$$\varphi|_{\Sigma_M^*} - \varphi|_{\Sigma_M^{\text{BL}}} = U_M^* \quad \text{and} \quad \varphi|_{\Sigma_E^*} - \varphi|_{\Sigma_E^{\text{BL}}} = U_E^* . \quad (77)$$

The whole potential drop between the bulk metal and the bulk electrolyte is thus

$$\varphi|_{\Sigma_M^*} - \varphi|_{\Sigma_E^*} = U_M^* + U_M^{\text{BL}} + U_E^{\text{BL}} + U_E^* =: U_{M,E} . \quad (78)$$

In a three electrode setup, this is related to the measurable voltage E via [15]

$$E = U_M^* + U_M^{\text{BL}} + U_E^{\text{BL}} + U_E^* + U_{E,R} , \quad (79)$$

where $U_{E,R}$ covers the whole electrolyte-reference potential drop. However, it is a quite common and valid assumption that $U_{E,R}$ is constant, which can be achieved experimentally very precisely [26].

Experimentally it is only possible to *vary* E and not each *individual* potential drop of eq. (79). However, there experimentally as well as theoretically there are some strategies to overcome this problem. For example, if the conductivity of the bulk phases Ω_E^* and Ω_M^* is very high, the potential drops U_E^* and U_M^* vanish.

5 Material functions

We restrict the further modeling procedure to an electrode/electrolyte interface with specified material functions.

5.1 Chemical potentials

5.1.1 Electrolyte

For the electrolyte phase, we rely on the free energy density $\rho\psi^E$ given in [15] which covers the entropy of mixing, solvation effects as well as the incompressibility of the liquid mixture. The chemical potentials of the respective constituents are

$$\mu_\alpha = g_\alpha^R + k_B T \ln y_\alpha + v_\alpha^R (p - p^E) \quad \alpha = 0, 1, \dots, N_E, \quad (80)$$

where g_α^R denotes the reference partial molar Gibbs energy, $y_\alpha = \frac{n_\alpha}{n}$ the mole fraction, $n = \sum_{\alpha=0}^N n_\alpha$ the number density of mixing particles², v_α^R the partial molar volume, and p is the pressure. Note that the incompressibility of the liquid mixture implies the constraint

$$n = \frac{1}{\sum_{\alpha=0}^N v_\alpha^R y_\alpha}. \quad (81)$$

For the following derivation we assume that upon the equilibrium assumption of the dissociation reactions the reaction rates r_α (and thus also r_α^{DL}) vanish.

5.1.2 Electrode

The electrode is considered as a mixture of electrons e^- , metal ions M , and additional constituents \mathcal{I}_M^a which can be *dissolved* in the metallic lattice (e.g. intercalated, solution solution, etc.). For the electrons and the metal ions we rely on a Thomas–Fermi electron gas with free energy density $\rho\psi^M$ of [15], leading to representations

$$\mu_M = \psi_M^R + v_M^R p_M + k_B T \ln a_M \quad \text{and} \quad \mu_e = \frac{h^2}{2m_e} \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} n_e^{\frac{2}{3}}, \quad (82)$$

where v_M^R denotes the partial molar volume of the metal ions, p_M the metal ion partial pressure, ψ_M^R the reference molar free energy, and a_M the activity of the metal ions. The incompressibility implies $v_M^R = 1/n_M$.

For the additional species we write simply

$$\mu_\alpha = \psi_\alpha^R + k_B T \ln a_\alpha \quad \alpha \in \mathcal{I}_M^a, \quad (83)$$

where a_α is the activity. If $\mathcal{I}_M^a = \emptyset$ we have $a_M = 1$. Various models for the activity and thus the state of an ion or an intercalated species in a solid exists [13, 27–30] and can be directly applied. However, for the further derivation we do not want to specify the material model further.

²Note that due to the solvation effect not all solvent molecules participate in the entropy of mixing. Since each ion binds κ_α solvent molecules, n_0 actually denotes the *free* solvent molecules, while $n_0^t = n_0 + \sum_{\alpha=1}^N \kappa_\alpha n_\alpha$ denotes the *total* number density of solvent in the mixture.

5.1.3 Surface

For the electrode surface Σ we consider a surface free energy density ψ_s which covers surface solvation effects, surface incompressibility, entropy of mixing, and reference contributions [15]. With the explicit representation of ψ_s given in [15] we obtain the surface chemical potentials

$$\mu_\alpha = \begin{cases} \psi_s^R + k_B T \ln y_\alpha - \bar{\omega}_\alpha k_B T \ln y_V & \text{for } \alpha \in \mathcal{I}_s \setminus \{e^-, M\} \\ \psi_s^R + \bar{\omega}_M k_B T \ln y_V - a_M^R \gamma_s^E & \text{for } \alpha = M \\ \psi_e^R = \text{const.} & \text{for } \alpha = e^- . \end{cases} \quad (84)$$

The respective quantities are

- the number of surface vacancies

$$n_s^V = \bar{\omega}_M n_M - \sum_{\alpha=0}^{N_S} \bar{\omega}_\alpha n_\alpha , \quad (85)$$

where $\bar{\omega}_\alpha$ denotes the number of adsorption sites of A_α ,

- the number of mixing particles

$$n_s = n_s^V + \sum_{\alpha=0}^{N_S} n_\alpha , \quad (86)$$

- the surface fractions

$$y_\alpha = \frac{n_\alpha}{n_s} , \quad \alpha = 0, 1, \dots, N_S, V , \quad (87)$$

- the adsorbate surface tension γ_s^E ,
- the partial molar area of the metal surface a_M^R ,
- and the constant electron surface chemical potential ψ_e^R .

The surface incompressibility implies quite similar to (81) the constraint

$$n_M = \frac{1}{a_M^R} \Leftrightarrow a_V^R n_V + \sum_{\alpha=0}^{N_S} a_\alpha^R n_\alpha = 1 \quad (88)$$

with the partial molar areas

$$a_V^R = \frac{1}{\bar{\omega}_M} a_M^R \quad \text{and} \quad a_\alpha^R = \frac{\bar{\omega}_\alpha}{\bar{\omega}_M} a_M^R = \bar{\omega}_\alpha a_V^R . \quad (89)$$

5.2 Equilibrium representations and consequences

5.2.1 Electrolyte boundary layer

The equilibrium conditions (30) of the electrolytic boundary layer Ω_E^{BL} lead to the representations

$$y_\alpha = y_\alpha \Big|_E^{\text{BL}} \cdot e^{-\frac{z_\alpha e_0}{k_B T} u - \frac{v_\alpha^R}{k_B T} \hat{p}(u)} = \hat{y}_\alpha(u) \quad (90)$$

where $\hat{p}(u)$ is obtained from the implicit equation system

$$g(u, p) = \sum_{\alpha \in \mathcal{I}_E} y_\alpha - 1 = 0 . \quad (91)$$

Together with (81) we have thus a representation

$$\hat{n}_\alpha(u) = \frac{y_\alpha \Big|_E^{\text{BL}} \cdot e^{-\frac{z_\alpha e_0}{k_B T} u - \frac{v_\alpha^R}{k_B T} \hat{p}(u)}}{\sum_{\beta=0}^N v_\beta^R \cdot y_\beta \Big|_E^{\text{BL}} \cdot e^{-\frac{z_\beta e_0}{k_B T} u - \frac{v_\beta^R}{k_B T} \hat{p}(u)}} , \quad \alpha \in \mathcal{I}_E . \quad (92)$$

The coupled Poisson-momentum equation system

$$\varepsilon_0 \operatorname{div} (1 + \chi) \mathbf{E} = q_i \quad \text{and} \quad \nabla p \cdot \mathbf{b}_u = q_i \mathbf{E} \cdot \mathbf{b}_u = q_i E_u \quad (93)$$

leads to the representation [15]

$$\hat{E}_u(u) = \operatorname{sgn}(u) \sqrt{\frac{2}{\varepsilon_0(1 + \chi_E)}} \hat{p}(u) . \quad (94)$$

Hence we have the necessary representations $\hat{n}_\alpha(u)$ and $\hat{E}_u(u)$ stated in section 2.3 to compute

$$n_\alpha^{\text{BL}} = \int_0^{U_E^{\text{BL}}} \hat{n}_\alpha \frac{1}{|E_u|} du = \hat{n}_\alpha^{\text{BL}}(U_E^{\text{BL}}) . \quad (95)$$

However, since actually only derivatives of n_α^{BL} with respect to U_E^{BL} arise in the boundary conditions (131), we obtain

$$C_\alpha^{\text{BL}} = \frac{dn_\alpha^{\text{BL}}}{dU_E^{\text{BL}}} = \frac{\hat{y}_\alpha(U_E^{\text{BL}})}{\sum_{\beta \in \mathcal{I}_E} v_\beta^R \cdot \hat{y}_\beta(U_E^{\text{BL}})} \left(\frac{2}{\varepsilon_0(1 + \chi_E)} \hat{p}(U_E^{\text{BL}}) \right)^{-\frac{1}{2}} . \quad (96)$$

The boundary layer capacity (73) has then the representation

$$C_E^{\text{BL}} = -\operatorname{sgn}(\varphi - \varphi^E) \sqrt{\frac{\varepsilon_0(1 + \chi_E)}{2(\hat{p}(U_E^{\text{BL}}))}} \cdot q_E(U_E^{\text{BL}}, \hat{p}(U_E^{\text{BL}})) . \quad (97)$$

5.2.2 Electrode potential drop

The equilibrium adsorption condition for the electrons, namely $\mu_e = \mu_e|_M^{\text{BL}} - e_0 U_M^{\text{BL}}$, actually entails

$$U_M^{\text{BL}} = \text{const.} \quad (98)$$

since $\mu_e = \text{const.}$ This condition thus describes the metallic behavior of an electrode, where $U_M^{\text{BL}} = \text{const.}$ implies that any excess charge on the electrode is excessively stored on the surface in terms of surface electrons. We refer to [15] for a detail discussion on this aspect. It is to emphasize, however, that for non-metallic/electrolyte interfaces U_M^{BL} is not necessarily a constant. The electro-neutrality condition along the arc γ gives then some implicit equation $F(U_E^{\text{BL}}, U_M^{\text{BL}}) = 0$ with which one could proceed. However, this requires a careful derivation based on the equations stated above.

For our purpose here we proceed with the condition $U_M^{\text{BL}} = \text{const.}$. In the boundary condition (131) the term $\frac{dU_M^{\text{BL}}}{dt}$ thus vanishes and $C_\alpha^{\text{Pseu}, M}$ does not contribute.

5.2.3 Adsorbates

The adsorption equilibrium conditions (38) for $\alpha \in \mathcal{I}_{\text{EM}}$ and surface reaction equilibrium conditions (41) for the constituents A_α , $\alpha \in \mathcal{I}_s^e$ lead to representations [15]

$$y_\alpha = \hat{y}_\alpha(U_E^{\text{BL}}, \gamma_E) \quad \alpha \in \mathcal{I}_s \quad (99)$$

$$n_\alpha = \frac{y_\alpha}{a_V^R y_V + \sum_{\beta \in \mathcal{I}_s} a_\beta^R y_\beta} \quad \alpha \in \mathcal{I}_s \quad (100)$$

together with the constraint

$$g(U_E^{\text{BL}}, \gamma_E) = y_V + \sum_{\alpha \in \mathcal{I}_s} y_\alpha - 1 = 0 \quad (101)$$

which satisfies

$$\frac{d\gamma_E}{dU_E^{\text{BL}}} = q_s. \quad (102)$$

This determines (for $\alpha \in \mathcal{I}_s$)

$$C_\alpha = \frac{dn_\alpha}{dU_E} = \frac{\partial n_\alpha}{\partial U_E} + q_s \frac{\partial n_\alpha}{\partial \gamma_E} \quad (103)$$

$$= -\frac{e_0}{k_B T a_V^R} \left(\frac{f_1 \cdot f_4 - f_3 \cdot f_2}{(f_2)^2} + \frac{f_1 f_4 \cdot f_2 - f_1 \cdot f_5}{f_2 (f_2)^2} \right) = \hat{C}_\alpha(U_E^{\text{BL}}) \quad (104)$$

with the (dimensionless) abbreviations

$$f_1 := y_\alpha, \quad f_2 := y_V + \sum_{\alpha \in \mathcal{I}_S} \omega_\alpha y_\alpha, \quad f_3 = z_\alpha y_\alpha \quad (105)$$

$$f_4 = e_0 \sum_{\alpha \in \mathcal{I}_S} z_\alpha \omega_\alpha y_\alpha, \quad f_5 = y_V + \sum_{\alpha \in \mathcal{I}_S} \omega_\alpha^2 y_\alpha, \quad (106)$$

and consequently

$$C_\alpha^{\text{Pseu,E}} = \frac{d}{dU_E^{\text{BL}}} \left(\sum_{\beta \in \mathcal{I}_S^e} \nu_{\beta,\alpha} n_\beta \right) = \hat{C}_\alpha^{\text{Pseu,E}}(U_E^{\text{BL}}). \quad (107)$$

Note that this leads to explicit expressions of the surface capacity

$$C_s^{\text{E}} = \frac{dq_E}{dU_E^{\text{BL}}} = e_0 \frac{d}{dU_E^{\text{BL}}} \sum_{\alpha \in \mathcal{I}_E} z_\alpha n_\alpha \quad (108)$$

and the electrolytic *pseudo*-capacity

$$C_E^{\text{Pseu,E}} = \frac{dq_E^{\text{Pseu}}}{dU_E^{\text{BL}}} = e_0 \frac{d}{dU_E^{\text{BL}}} \sum_{\alpha \in \mathcal{I}_S^e} z_\alpha^{\text{E}} n_\alpha. \quad (109)$$

5.3 Reaction rates of transfer reactions

Based on the chemical potentials specified in the section 5.1 we can now also deduce explicit representations of the reaction rates R_β^T (eq. (47)) for the transfer reactions (43).

However, some preliminary abbreviations are useful for the further derivation:

$$\pi_\beta \Big|_{\text{E}}^{\text{BL}} := \frac{1}{y_\beta \Big|_{\text{E}}^{\text{BL}}} \prod_{\alpha \in \mathcal{I}_E \setminus \{\alpha\}} (y_\alpha \Big|_{\text{E}}^{\text{BL}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_M \setminus \text{e}^-} (a_\alpha \Big|_{\text{M}}^{\text{BL}})^{\nu_{\alpha,\beta}}, \quad \beta \in \mathcal{I}_E^r \quad (110)$$

$$\pi_\beta \Big|_{\text{M}}^{\text{BL}} := \frac{1}{a_\beta \Big|_{\text{M}}^{\text{BL}}} \prod_{\alpha \in \mathcal{I}_E} (y_\alpha \Big|_{\text{E}}^{\text{BL}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_M \setminus \{\alpha, \text{e}^-\}} (a_\alpha \Big|_{\text{M}}^{\text{BL}})^{\nu_{\alpha,\beta}}, \quad \beta \in \mathcal{I}_M^r. \quad (111)$$

Some auxiliary calculations then lead to the representations

$$R_\beta^T = L_\beta^T \cdot \left(\left(\pi_\beta \Big|_{\text{E}}^{\text{BL}} \right)^{\alpha_\beta} \cdot \text{e}^{-\alpha_\beta \cdot \left(\frac{\Delta g_\beta^T}{k_B T} + z_\beta^{\text{M}} \frac{e_0}{k_B T} U_E^{\text{BL}} \right)} - \left(\pi_\beta \Big|_{\text{E}}^{\text{BL}} \right)^{-(1-\alpha_\beta)} \text{e}^{(1-\alpha_\beta) \cdot \left(\frac{\Delta g_\beta^T}{k_B T} + z_\beta^{\text{M}} \frac{e_0}{k_B T} U_E^{\text{BL}} \right)} \right) = \hat{R}_\beta^T(U_E^{\text{BL}}) \quad \beta \in \mathcal{I}_E^r \quad (112)$$

$$R_\beta^T = L_\beta^T \cdot \left(\left(\pi_\beta \Big|_{\text{M}}^{\text{BL}} \right)^{\alpha_\beta} \cdot \text{e}^{-\alpha_\beta \cdot \left(\frac{\Delta g_\beta^T}{k_B T} - z_\beta^{\text{E}} \frac{e_0}{k_B T} U_E^{\text{BL}} \right)} - \left(\pi_\beta \Big|_{\text{M}}^{\text{BL}} \right)^{-(1-\alpha_\beta)} \text{e}^{(1-\alpha_\beta) \cdot \left(\frac{\Delta g_\beta^T}{k_B T} - z_\beta^{\text{E}} \frac{e_0}{k_B T} U_E^{\text{BL}} \right)} \right) = \hat{R}_\beta^T(U_E^{\text{BL}}) \quad \beta \in \mathcal{I}_M^r \quad (113)$$

with

$$\Delta g_\beta^T = \begin{cases} g_\beta^R - \sum_{\alpha \in \mathcal{I}_{EM} \setminus \{\beta\}} \nu_{\alpha,\beta} g_\alpha^R - e_0 z_\beta^M U_M^{BL}, & \text{for } \beta \in \mathcal{I}_E^r \\ g_\beta^R - \sum_{\alpha \in \mathcal{I}_{EM} \setminus \{\beta\}} \nu_{\alpha,\beta} g_\alpha^R + e_0 z_\beta^E U_M^{BL} & \text{for } \beta \in \mathcal{I}_M^r \end{cases}. \quad (114)$$

Note, however, that the incorporation of the boundary layer potential drop U_M^{BL} in the definition of Δg_β^T is only useful when $U_M^{BL} = \text{const.}$ For a semiconductor-electrolyte or an electrolyte-electrolyte interface this is not necessarily the case.

5.4 Balance equations and boundary conditions

At this stage it is quite illustrative to briefly summarize the derivation and the general results. We shifted the boundary layer contributions of the balance equations (14) into the new boundary conditions (22) at Σ^{DL} which gives the balance equations

$$\frac{\partial n_\alpha}{\partial t} = -\text{div}(\mathbf{j}_\alpha) + r_\alpha \quad \mathbf{x} \in \Omega_i^*, \alpha \in \mathcal{I}_i, i = E, M, \quad (115)$$

in the electro-neutral domains Ω_i^* . We have thus $q_i = 0$ in Ω_i^* which reduces the charge balance to

$$\text{div} \mathbf{J}_{q_i} = 0 \quad \mathbf{x} \in \Omega_i^*. \quad (116)$$

The boundary conditions at the interface Σ^{DL} are, based on the specific material functions of this section,

■ for the **Electrolyte species**,

$$\mathbf{j}_\alpha \cdot \mathbf{n}|_E^{BL} = \begin{cases} C_\alpha^{\text{Eff}} \cdot \frac{dU_E^{BL}}{dt} + \sum_{\beta \in \mathcal{I}_{EM}^r} \nu_{\beta,\alpha} R_\beta^T + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_E' \\ C_\alpha^{\text{Eff}} \cdot \frac{dU_E^{BL}}{dt} - R_\alpha^T + \sum_{\beta \in \mathcal{I}_{EM}^r \setminus \{\alpha\}} \nu_{\beta,\alpha} R_\beta^T + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_E^r \end{cases} \quad (117)$$

■ and for the **Metal species**,

$$-\mathbf{j}_\alpha \cdot \mathbf{n}|_M^{BL} = \begin{cases} C_\alpha^{\text{Pseu},E} \cdot \frac{dU_E^{BL}}{dt} + \sum_{\beta \in \mathcal{I}_{EM}^r} \nu_{\beta,\alpha} R_\beta^T + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_M' \\ C_\alpha^{\text{Pseu},E} \cdot \frac{dU_E^{BL}}{dt} - R_\alpha^T + \sum_{\beta \in \mathcal{I}_{EM}^r \setminus \{\alpha\}} \nu_{\beta,\alpha} R_\beta^T + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_M^r \end{cases}. \quad (118)$$

The incompressibility constraint

$$\sum_{\alpha \in \mathcal{I}_E} v_\alpha^R n_\alpha = 1 \quad \text{and} \quad v_M^R n_M = 1 \quad (119)$$

can be used to obtain an equation for the barycentric velocity, namely

$$\sum_{\alpha \in \mathcal{I}_E} v_\alpha^R \frac{\partial n_\alpha}{\partial t} = -\text{div} \mathbf{v} = 0 \quad \text{and} \quad v_M^R \frac{\partial n_M}{\partial t} = -\text{div} \mathbf{v} = 0 \quad (120)$$

Note that the boundary condition for the normal component of the barycentric velocity is determined from

$$n\mathbf{v} \cdot \mathbf{n} \Big|_i^{\text{BL}} = \sum_{\alpha \in \mathcal{I}_i} \mathbf{j}_\alpha \cdot \mathbf{n} \Big|_i^{\text{BL}} \quad i = \text{E}, \text{M} . \quad (121)$$

At the respective bulk surfaces Σ_{E}^* and Σ_{M}^* we fix the concentration of all species, i.e.

$$n_\alpha \Big|_{\Sigma_i^*} = n_\alpha^i \quad \alpha \in \mathcal{I}_i , \quad i = \text{E}, \text{M} . \quad (122)$$

5.5 Initial conditions

At the *beginning* of any experiment we want to prescribe a homogenous concentration throughout the domains Ω_i^* , $i = \text{E}, \text{M}$. We have thus the initial conditions

$$n_\alpha(\mathbf{x}, 0) = n_\alpha^i \quad \mathbf{x} \in \Omega_i^* , \alpha \in \mathcal{I}_i , \quad i = \text{E}, \text{M}, \quad (123)$$

in order to be compatible to the boundary condition (122). Further we consider that no tangential diffusional fluxes occur.

But what about the initial *reaction* conditions at the interface Σ^{DL} ?

Let $U_{\text{E}}^{\text{BL}}(t=0) = U_{\text{E}}^{\text{BL},0}$ be the applied potential difference at $t=0$. We can evaluation the π -functions (110) with the bulk concentrations n_α^i , namely

$$\pi_\beta^{\text{E}} := \frac{1}{y_\beta^{\text{E}}} \prod_{\alpha \in \mathcal{I}_{\text{E}} \setminus \{\alpha\}} (y_\alpha^{\text{E}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_{\text{M}} \setminus \text{e}^-} (a_\alpha^{\text{M}})^{\nu_{\alpha,\beta}} \quad \beta \in \mathcal{I}_{\text{E}}^r , \quad (124)$$

$$\pi_\beta^{\text{M}} := \frac{1}{a_\beta^{\text{M}}} \prod_{\alpha \in \mathcal{I}_{\text{E}}} (y_\alpha^{\text{E}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_{\text{M}} \setminus \{\alpha, \text{e}^-\}} (a_\alpha^{\text{M}})^{\nu_{\alpha,\beta}} \quad \beta \in \mathcal{I}_{\text{M}}^r . \quad (125)$$

Consider now the transfer reactions at time $t=0$, i.e. for $\beta \in \mathcal{I}_i^r, i, j = \text{E}, \text{M}, i \neq j$

$$R_\beta^T \Big|_{U_{\text{E}}^{\text{BL},0}} = L_\beta^T \cdot \left((\pi_\beta^i)^{\alpha_\beta} \cdot \text{e}^{-\alpha_\beta \cdot \left(\frac{\Delta g_\beta^T}{k_{\text{B}} T} + z_\beta^j \frac{e_0}{k_{\text{B}} T} U_{\text{E}}^{\text{BL},0} \right)} - (\pi_\beta^i)^{-(1-\alpha_\beta)} \text{e}^{(1-\alpha_\beta) \cdot \left(\frac{\Delta g_\beta^T}{k_{\text{B}} T} + z_\beta^j \frac{e_0}{k_{\text{B}} T} U_{\text{E}}^{\text{BL},0} \right)} \right) =: R_\beta^{T,0} . \quad (126)$$

For given values of the Δg_β^T in eq. (112) these are in general not equal to zero and could entail a *huge* flux at time $t=0$ through the interface. This is actually the exchange current density $j_\alpha^{0,T}$ of the constituent A_α due to the transfer reactions, with

$$j_\alpha^{0,T} = \begin{cases} \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta,\alpha} R_\beta^{T,0} , & \text{if } \alpha \in \mathcal{I}_{\text{EM}}' \\ -R_\alpha^{T,0} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta,\alpha} R_\beta^{T,0} , & \text{if } \alpha \in \mathcal{I}_{\text{EM}}^r . \end{cases} \quad (127)$$

We may thus re-define the total flux as

$$\mathbf{i}_\alpha := \mathbf{j}_\alpha - j_\alpha^{0,T} \mathbf{n} \quad (128)$$

which satisfies the balance equation

$$\frac{\partial n_\alpha}{\partial t} = -\text{div } \mathbf{i}_\alpha + r_\alpha \quad \mathbf{x} \in \Omega_i^*, \alpha \in \mathcal{I}_i, i = \text{E, M}, \quad (129)$$

and is subject to the boundary conditions

■ **Electrolyte species,**

$$\mathbf{i}_\alpha \cdot \mathbf{n}|_{\text{E}}^{\text{BL}} = \begin{cases} C_\alpha^{\text{Eff}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta, \alpha} (R_\beta^T - R_\beta^{T,0}) + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}'_{\text{E}} \\ C_\alpha^{\text{Eff}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta, \alpha} (R_\beta^T - R_\beta^{T,0}) \\ \quad - (R_\alpha^T - R_\alpha^{T,0}) + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_{\text{E}}^r \end{cases} \quad (130)$$

■ **Metal species,**

$$-\mathbf{i}_\alpha \cdot \mathbf{n}|_{\text{M}}^{\text{BL}} = \begin{cases} C_\alpha^{\text{Pseu, E}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta, \alpha} (R_\beta^T - R_\beta^{T,0}) + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}'_{\text{M}} \\ C_\alpha^{\text{Pseu, E}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta, \alpha} (R_\beta^T - R_\beta^{T,0}) \\ \quad - (R_\alpha^T - R_\alpha^{T,0}) + \text{div}_s \mathbf{J}_\alpha^{\text{Eff}} & \alpha \in \mathcal{I}_{\text{M}}^r. \end{cases} \quad (131)$$

This *new* total flux satisfies then the initial reaction conditions

$$\mathbf{i}_\alpha \cdot \mathbf{n}|_{\text{E}}^{\text{BL}} = C_\alpha^{\text{Eff}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} \quad \alpha \in \mathcal{I}_{\text{E}} \quad (132)$$

and

$$-\mathbf{i}_\alpha \cdot \mathbf{n}|_{\text{M}}^{\text{BL}} = C_\alpha^{\text{Pseu, E}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} \quad \alpha \in \mathcal{I}_{\text{M}}. \quad (133)$$

Note that this gives also rise to an **transfer current density** $I^{T,0}$ as

$$i^{T,0} = e_0 \sum_{\alpha \in \mathcal{I}_{\text{M}}^r} z_\alpha^{\text{E}} R_\alpha^{T,0} - e_0 \sum_{\alpha \in \mathcal{I}_{\text{E}}^r} z_\alpha^{\text{M}} R_\alpha^{T,0} \quad (134)$$

which can be computed from the above representations.

5.6 Flux relation

The most simple relation between the diffusional flux \mathbf{j}_α and the chemical potentials μ_α in order to ensure a non-negative entropy production is [13, 31]

$$\mathbf{J}_\alpha = D_\alpha n_\alpha \frac{1}{k_{\text{B}} T} \nabla \left(\mu_\alpha - \frac{m_\alpha}{m_{i,0}} \mu_{i,0} + e_0 z_\alpha - \frac{m_\alpha}{m_{i,0}} z_{i,0} \right) \varphi \quad \alpha \in \mathcal{I}_i \setminus \{A_{i,0}\}, i = \text{E, M}, \quad (135)$$

where $A_{i,0}$ is some *reference* species of the respective phase, e.g. the solvent in a liquid mixture or the lattice constituents in some solid.

A similar relation can be implied on the surface to relate the tangential surface flux \mathbf{J}_s^α to the surface chemical potentials μ_α . However, we in the following the

6 Flat inert metal/electrolyte interface

In order to validate the general modeling procedure, we employ some meaningful assumptions to simplify the overall equation system. We seek then to compute the current density/voltage relation $(i(t), E(t))$ based on the preceding model.

6.1 Electrode

The metal Ω_M is considered to consists only of two species, $\mathcal{I}_M = \{e^-, M\}$, where the metal M does not participate in any surface reaction. This corresponds to an inert electrode without intercalation. Further, we assumed the surface to be flat, which allows for a 1D approximation. The metal surface is positioned at x_s and the double layer is thus Σ^{DL} is (x_E^{BL}, x_M^{BL}) . The bulk metal is positioned at x_M^* and the bulk electrolyte at x_E^* . The conductivity of the metal is assumed to be sufficiently large to ensure $U_M^* = 0$.

6.2 Electrolyte

Reconsider the index set of electrolyte species, $\mathcal{I}_E = \mathcal{I}_E' \cup \mathcal{I}_E^r$. We can, however, introduce an additional decomposition

$$\mathcal{I}_E = \mathcal{I}_E^{Supp} \cup \mathcal{I}_E^{Act} \quad (136)$$

where \mathcal{I}_E^{Supp} denotes the **supporting electrolyte** species (in addition to the solvent) and \mathcal{I}_E^{Act} the **electro-active** constituents, i.e. reaction educts and products of the transfer reactions.

A supporting electrolyte (anions, cations, solvent, etc. with index set \mathcal{I}_E^{Supp}), in electrochemistry, according to the IUPAC definition, is an electrolyte containing chemical species that are not electro-active and have an ionic strength i_E^{Supp} and conductivity κ_E^{Supp} , i.e.

$$i_E^{Supp} = e_0 \sum_{\alpha \in \mathcal{I}_E^{Supp}} z_\alpha^2 n_\alpha \quad \text{and} \quad \kappa_E^{Supp} = e_0 \sum_{\alpha \in \mathcal{I}_E^{Supp}} (e_0 z_\alpha)^2 D_\alpha n_\alpha, \quad (137)$$

much larger than that of the electro-active species (dissolved gas, anions, cations, etc. with index set \mathcal{I}_E^{Act}). Supporting electrolyte is also sometimes referred to as inert electrolyte or inactive electrolyte and do not participate in transfer reactions.

For our general transfer reactions

$$\sum_{\alpha \in \mathcal{I}_{EM} \setminus \{\beta\}} \nu_{\alpha, \beta} A_\alpha \Big|_E^{BL} \rightleftharpoons A_\beta \Big|_E^{BL} \quad \forall \beta \in \mathcal{I}_{EM}^r \quad (138)$$

we can conclude ($\beta \in \mathcal{I}_{EM}^r$)

$$\nu_{\alpha, \beta} = 0 \quad \text{for} \quad \alpha \in \mathcal{I}_E^{Supp}, \quad \text{and} \quad \nu_{\alpha, \beta} \neq 0 \quad \text{for} \quad \alpha \in \mathcal{I}_E^{Act}. \quad (139)$$

The supporting electrolyte species are thus **not** taking part in the boundary conditions (130), whereby the balance equations decouple. It is thus sufficient to solve the PDE system

$$\frac{\partial n_\alpha}{\partial t} = -\partial_x j_\alpha \quad \text{for} \quad \alpha \in \mathcal{I}_E^{\text{Act}}. \quad (140)$$

In addition, the decomposition $\mathcal{I}_E = \mathcal{I}_E^{\text{Supp}} \cup \mathcal{I}_E^{\text{Act}}$ propagates also to the current

$$J_q = e_0 \sum_{\alpha \in \mathcal{I}_E} z_\alpha j_\alpha = J_q^{\text{Supp}} + J_q^{\text{Diff}}. \quad (141)$$

Note that in Ω_E^* we have $q_E = 0$ and thus

$$J_q = \text{const.} \quad (142)$$

The electric current J_q decomposes as

$$J_q = (\kappa_E^{\text{Supp}} + \kappa_E^{\text{Act}}) \partial_x \varphi + \kappa_E^{\text{Supp}} \cdot F_{\text{chem}}^{\text{Supp}} + \kappa_E^{\text{Act}} \cdot F_{\text{chem}}^{\text{Act}} \quad (143)$$

with

$$\kappa_E^i = e_0 \sum_{\alpha \in \mathcal{I}_E} (e_0 z_\alpha)^2 D_\alpha n_\alpha \quad i = \text{Supp, Act} \quad (144)$$

$$F_{\text{chem}}^i = e_0 \sum_{\alpha \in \mathcal{I}_E^i} z_\alpha \frac{D_\alpha}{\kappa_E^{\text{Supp}}} n_\alpha \nabla (\mu_\alpha - \frac{m_\alpha}{m_0} \mu_0) \quad i = \text{Supp, Act} \quad (145)$$

We assume now $\kappa_E^{\text{Supp}} \rightarrow \infty$, which implies

$$\partial_x \varphi \rightarrow 0 \quad \text{and thus} \quad U_E^* \rightarrow 0. \quad (146)$$

Supporting electrolytes are widely used in electrochemical measurements when control of electrode potentials is required, which is the sake of this study. The huge conductivity of the solution practically eliminates the so-called IR drop U_E^* in the bulk electrolyte Ω_E^* and thus simplifies the equation system (as well as the experimental access).

The flux of the electro-active species ($\alpha \in \mathcal{I}_E^{\text{Act}}$) reduces further to

$$j_\alpha = -D_\alpha n_\alpha \frac{1}{k_B T} \partial_x ((\mu_\alpha - \frac{m_\alpha}{m_0} \mu_0)) \quad (147)$$

Assuming further that the chemical diffusion is just a *simple* diffusion process, i.e.

$$j_\alpha = D_\alpha n_\alpha \frac{1}{k_B T} \partial_x ((\mu_\alpha - \frac{m_\alpha}{m_0} \mu_0)) \approx -D_\alpha \partial_x n_\alpha \quad \alpha \in \mathcal{I}_E^{\text{Act}}, \quad (148)$$

leads to the (simple) PDE system (for all $\alpha \in \mathcal{I}_E^{\text{Act}}$)

$$\frac{\partial n_\alpha}{\partial t} = -\partial_x i_\alpha \quad (149)$$

$$i_\alpha = -D_\alpha \partial_x n_\alpha. \quad (150)$$

Hence, the transfer reactions actually determine which balance equations require to be solved.

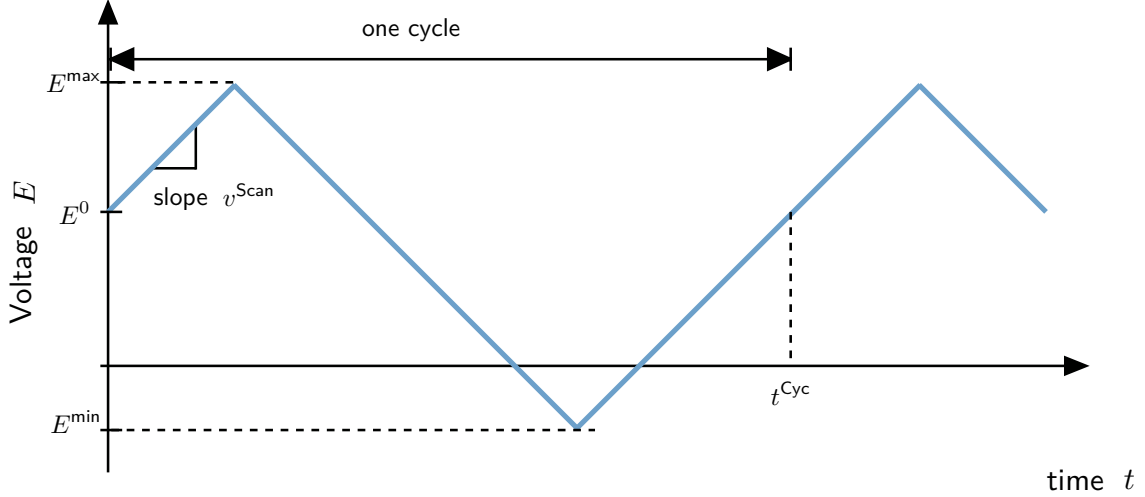


Figure 3: Time dependent Voltage $E(t)$ with scan rate v^{scan} , initial potential E^0 , potential maximum E^{max} and minimum E^{min} for one cycle with time length t^{Cycle} .

6.3 Current/Voltage relation

Based on our assumptions the measured current (69) is

$$i - i^{T,0} = C_{\text{E}}^{\text{Eff}} \cdot \frac{dU_{\text{E}}^{\text{BL}}}{dt} + e_0 \sum_{\alpha \in \mathcal{I}_{\text{E}}} z_{\alpha}^{\text{M}} (R_{\alpha}^T - R_{\alpha}^{T,0}) \quad (151)$$

which has capacitive contribution and a *Faradaic* contribution. Note, however, that an *evaluation* of this equation actually requires the (numerical) solutions $\tilde{n}_{\alpha}(x, t)$ of the equation system (149)–(149) with boundary conditions (130). The representation (112) shows that R_{α} is actually a function of $U_{\text{E}}^{\text{BL}}(t)$ and $\pi_{\beta}|_{\text{E}}^{\text{BL}}$, with

$$\pi_{\beta}|_{\text{E}}^{\text{BL}} = \frac{1}{y_{\beta}|_{\text{E}}^{\text{BL}}} \prod_{\alpha \in \mathcal{I}_{\text{E}} \setminus \{\alpha\}} (y_{\alpha}|_{\text{E}}^{\text{BL}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_{\text{M}} \setminus \text{e}^{-}} (a_{\alpha}|_{\text{M}}^{\text{BL}})^{\nu_{\alpha,\beta}}, \quad \beta \in \mathcal{I}_{\text{E}}^r. \quad (152)$$

The expressions $y_{\beta}|_{\text{E}}^{\text{BL}}$ are actually evaluations of the time dependent solutions \tilde{y}_{α} at the boundary x_{E}^{BL} . While all species \mathcal{I}_{E} of the electrolyte phase contribute to the double layer capacity $C_{\text{E}}^{\text{Eff}}$, only the electro-active species $\mathcal{I}_{\text{E}}^{\text{Act}}$ contribute to the Faradaic current $\sum_{\alpha \in \mathcal{I}_{\text{E}}^r} z_{\alpha}^{\text{M}} (R_{\alpha}^T - R_{\alpha}^{T,0})$.

For the applied voltage reconsider that we have a relation

$$E = U_{\text{E}}^{\text{BL}} + U^{\text{R}} \quad \text{with} \quad U^{\text{R}} = \text{const.} \quad (153)$$

We consider a time-dependent triangular function according to Fig. 3 for E .

6.4 Non-dimensionalization of the equation system

In order to solve the equation system numerically, some preliminary non-dimensionalizations and variable transformations are required.

Consider first the non-dimensionalization

$$\xi = \frac{x}{x_L}, \quad \tau = \frac{t}{t^{\text{Cyc}}} \quad \Delta \tilde{g}_\alpha^T = \frac{\Delta g_\alpha^T}{k_B T} \quad (154)$$

$$\varphi = \frac{e_0}{k_B T} U_E^{\text{BL}} \quad u_\alpha = \frac{n_\alpha}{n_\alpha^E} \quad w_\alpha = \ln u_\alpha, \quad (155)$$

which does hold true since $n_\alpha^E \neq 0 \forall \alpha \in \mathcal{I}_E^{\text{Act}}$. Note that this implies also

$$\frac{y_\alpha}{y_\alpha^E} = \frac{n_\alpha}{n_\alpha^E} = u_\alpha \quad (156)$$

since $n = n^E = n^R$ and entails

$$\frac{\pi_\beta|_E^{\text{BL}}}{\pi_\beta^E} = \frac{y_\beta^E}{y_\beta|_E^{\text{BL}}} \frac{\prod_{\alpha \in \mathcal{I}_E \setminus \{\alpha\}} (y_\alpha|_E^{\text{BL}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_M \setminus e^-} (a_\alpha|_M^{\text{BL}})^{\nu_{\alpha,\beta}}}{\prod_{\alpha \in \mathcal{I}_E \setminus \{\alpha\}} (y_\alpha^E)^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_M \setminus e^-} (a_\alpha^M)^{\nu_{\alpha,\beta}}} \quad (157)$$

$$= \frac{1}{u_\beta|_E^{\text{BL}}} \prod_{\alpha \in \mathcal{I}_E \setminus \{\alpha\}} (u_\alpha|_E^{\text{BL}})^{\nu_{\alpha,\beta}} \prod_{\alpha \in \mathcal{I}_M \setminus e^-} (u_\alpha|_M^{\text{BL}})^{\nu_{\alpha,\beta}} =: \tilde{\pi}_\beta|_E^{\text{BL}}. \quad (158)$$

Note, however, that it is numerically *problematic* to consider u_α as variable since these values might become negative due to the accumulation of numerical errors. However, using w_α as variable solves this problem and we have thus the following transformations:

$$\frac{\partial u_\alpha}{\partial t} = u_\alpha \frac{\partial w_\alpha}{\partial t} = e^{w_\alpha} \frac{\partial w_\alpha}{\partial t} \quad (159)$$

$$\partial_\xi u_\alpha = e^{w_\alpha} \partial_\xi w_\alpha \quad (160)$$

$$\tilde{\pi}_\beta|_E^{\text{BL}} = e^{\sum_{\alpha \in \mathcal{I}_{EM} \setminus \{\alpha, e^-\}} \nu_{\alpha,\beta} w_\alpha} e^{w_\beta|_E^{\text{BL}} - w_\beta|_E^{\text{BL}}}. \quad (161)$$

We obtain finally the following mathematical problem:

■ **PDE System:**

$$e^{w_\alpha} \frac{\partial w_\alpha}{\partial \tau} = \partial_\xi \tilde{i}_\alpha \quad \text{for } \alpha \in \mathcal{I}_E^{\text{Act}} \quad (162)$$

$$\tilde{i}_\alpha = \tilde{D}_\alpha e^{w_\alpha} \partial_\xi w_\alpha \quad (163)$$

with

$$\tilde{D}_\alpha = \frac{t^{\text{Cyc}}}{x_L^2} D_\alpha, \quad i_\alpha = -\tilde{d}_\alpha \tilde{i}_\alpha \quad \text{and} \quad \tilde{d}_\alpha = n_\alpha^E \frac{x_L}{t^{\text{Cyc}}}. \quad (164)$$

■ **bulk boundary condition** at x_E^* :

$$w_\alpha|_{x_E^*} = 0 \quad \text{for } \alpha \in \mathcal{I}_E^{\text{Act}}, \quad (165)$$

■ **transfer reaction conditions** at the double layer interface x_E^{DL} :

$$\tilde{i}_\alpha|_{\text{E}}^{\text{BL}} = \frac{1}{\tilde{d}_\alpha} \left(C_\alpha^{\text{Eff}} \cdot \frac{dE}{dt} + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r} \nu_{\beta,\alpha} \tilde{R}_\beta^T \right) \quad \alpha \in \mathcal{I}_{\text{E}}^r \cap \mathcal{I}_{\text{E}}^{\text{Act}} \quad (166)$$

$$\tilde{i}_\alpha|_{\text{E}}^{\text{BL}} = \frac{1}{\tilde{d}_\alpha} \left(C_\alpha^{\text{Eff}} \cdot \frac{dE}{dt} - \tilde{R}_\alpha^T + \sum_{\beta \in \mathcal{I}_{\text{EM}}^r \setminus \{\alpha\}} \nu_{\beta,\alpha} \tilde{R}_\beta^T \right) \quad \alpha \in \mathcal{I}_{\text{E}}^r \cap \mathcal{I}_{\text{E}}^{\text{Act}} \quad (167)$$

with $\tilde{R}_\beta = (R_\beta^T - R_\beta^{T,0})$

■ **initial conditions**

$$w_\alpha(0, x) = 0 \quad \alpha \in \mathcal{I}_{\text{E}} \quad (168)$$

After solving the PDE system, the solutions for u_α are obtained from

$$u_\alpha = e^{w_\alpha} . \quad (169)$$

6.5 Parameters

Before discussing the actual examples, it is illustrative to discuss briefly the parameters of the overall model framework.

6.5.1 Cyclic Voltammetry

The parameters for the cyclic voltammetry are the initial potential E^0 , the potential maximum E^{max} and the the minimum E^{min} , with $E^{\text{max}} - E^{\text{min}} \in [1 - 4]$ V. The scan rate v^{scan} is normally in the range of $10 - 100$ [Vs⁻¹]. Hence, the cycle time t^{Cyc} is normally in the order of 100s, and the number of cycles is denoted by N^{Cyc} .

6.5.2 Transport equations

The Diffusion coefficients D_α of the electro-active species $\mathcal{I}_{\text{E}}^{\text{Act}}$ dissolved in water are in the order of 10^{-5} [cm² s⁻¹]. For the computational domain $(x_{\text{E}}^{\text{BL}}, x_{\text{E}}^*)$ with $x_L = x_{\text{E}}^* - x_{\text{E}}^{\text{BL}}$ we employ a scaling with the Nernstian diffusion layer [2], which leads to

$$x_L = N_{\text{ND}} \cdot \sqrt{\max D_\alpha \cdot t^{\text{Cycle}} \cdot 10^4} \quad [\mu\text{m}] \quad (170)$$

and $N_{\text{ND}} = 5$ (conservative).

6.5.3 Capacity

Several parameter have an impact on the effective capacity C_E^{Eff} , and we refer to [15] for a detailed discussion on the respective values. Briefly summarized, the parameters are

$$\text{particle density at the boundary layer } n_\alpha \Big|_E^{\text{BL}}, \quad (171)$$

$$\text{charge numbers } z_\alpha, \quad \text{dielectric susceptibility } \chi_E,$$

$$\text{solvation numbers } \kappa_\alpha \text{ and } \kappa_s, \quad \text{adsorption energy } \Delta g_\alpha^A,$$

$$\text{partial molar volumes } v_\alpha^R, \quad \text{partial molar areas } a_\alpha^R.$$

In the examples section we provide explicit values without any further discussion.

6.5.4 Transfer reactions

For each transfer reaction (43) with reaction rate R_β^T we have essentially two parameters, L_β [molcm⁻²s] and Δg_β^T [eV] with $\Delta g_\beta^T \in (-2, 2)$ / eV.

The exchange current density for each reaction is then

$$i_\beta^0 = e_0 z_\beta^M L_\beta^T \cdot \left((\pi_\beta^i)^{\alpha_\beta} \cdot e^{-\alpha_\beta \cdot (\frac{\Delta g_\beta^T}{k_B T} + z_\beta^j \frac{e_0}{k_B T} U_E^{\text{BL},0})} - (\pi_\beta^i)^{-(1-\alpha_\beta)} e^{(1-\alpha_\beta) \cdot (\frac{\Delta g_\beta^T}{k_B T} + z_\beta^j \frac{e_0}{k_B T} U_E^{\text{BL},0})} \right), \quad (172)$$

which is in the order of / μAcm⁻². Note that parametric dependency of the transfer reaction and the resulting current on L_β and Δg_β^T is highly non-linear.

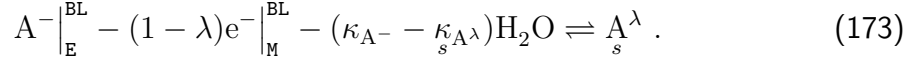
6.6 Examples

The scan rate is fixed for all examples as $v^{\text{Scan}} = 100 / \text{mV s}^{-1}$. If not mentioned otherwise, $E_0 = 0\text{V}$, $E^{\text{max}} = 1.5\text{V}$ and $E^{\text{min}} = -1.5\text{V}$.

6.6.1 ACsolution without transfer reaction

This first example servers to investigate the capacitive current. We consider now an aqueous solution of AC, which is completely dissociated into C⁺ and A⁻ ions. We employ the standard parameters of [15] and $\chi_E = 45$ for water and $v_{A^-}^R = v_{C^+}^R = 45 \cdot v_0^R$, where $v_0^R = 0.0180 / \text{L mol}^{-1}$ is the partial molar volume of water. The partial molar area of water is $a_0^R = 10.33 \cdot 10^8 / \text{cm}^2 \text{mol}^{-1}$ [15, 24]. The metal surface is considered as Ag₍₁₁₀₎.

The anion A^- may adsorb on the surface and thereby lose a part of the solvation shell as well as some partial charge, i.e.



This adsorption process entails that the partial molar area $a_{A^\lambda}^R$ of is related to λ [24]. We can thus perform a parameter variation of $a_{A^\lambda}^R$ for an aqueous AC solution and study the impact on the capacitive current density

$$i = C_E^{\text{Eff}} \cdot \frac{dE}{dt} . \quad (174)$$

The adsorption energy for A_s^λ is $\Delta g_{A^\lambda}^A = -0.2 / \text{eV}$.

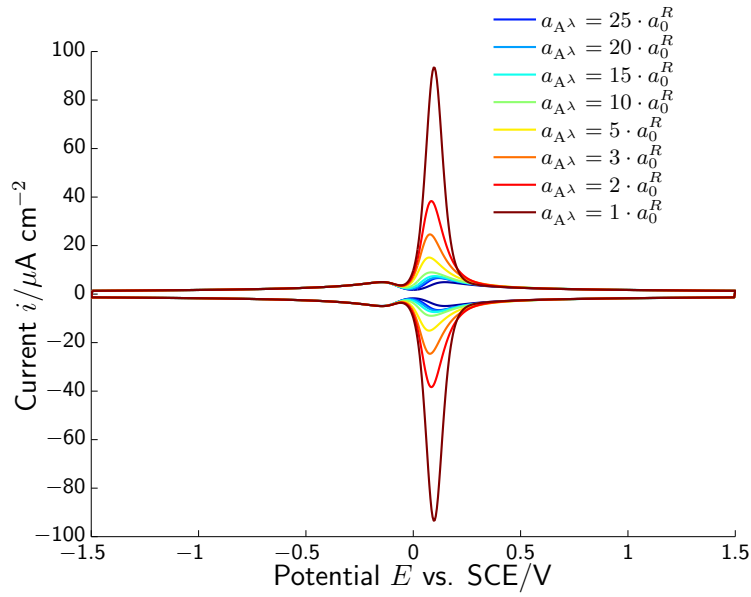
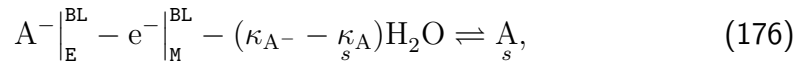
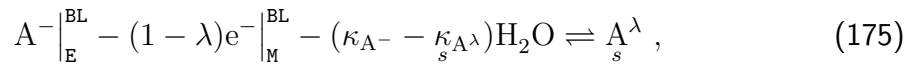


Figure 4: Numerical simulation of the capacitive current with adsorption and partial charge transfer reaction (175). The partial molar area of $a_{A^\lambda}^R$ on the surface is varied in multiples of a_0^R .

Note, however, that adsorption and discharge process could also be a 2-step mechanism, for example



where the uncharged reaction product A has solvation number $\kappa_A = 0$ and thus approximately $a_A^R = a_0^R$. Figure 5 shows a computation of the corresponding CV with $a_{A^\lambda}^R = 5 \cdot a_0^R$, $\Delta g_{A^\lambda}^A = -0.2 \text{eV}$ and a variation of Δg_A^A .

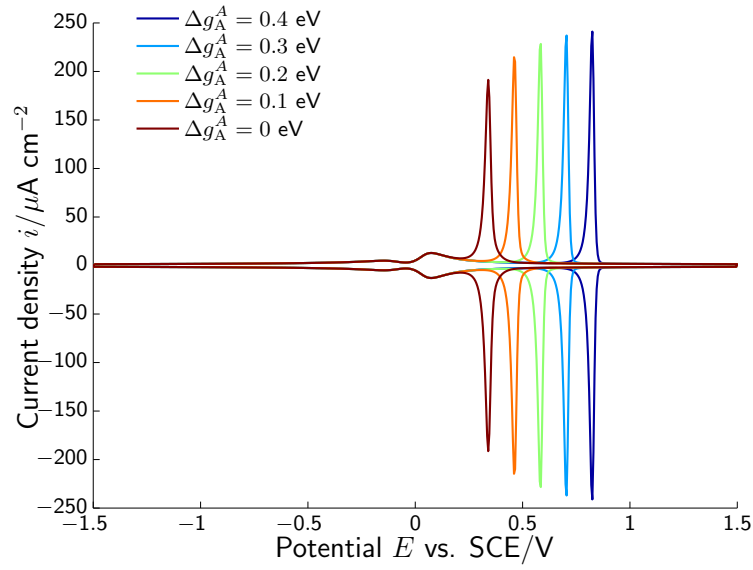


Figure 5: Numerical simulation of the capacitive current with two-step discharge of the anion A^- .

6.6.2 AC solution with transfer reaction

Next we consider an additional transfer reaction



for the example preceding example. The bulk concentration of n_C^E is set to $10^{-8} / \text{mol L}^{-1}$. The parameters for the transfer reactions are exemplarily chosen as $\Delta g_C^T = 0 / \text{eV}$ and $L\beta^T = 1.0364 \cdot 10^{-14} / \text{molm}^{-2}$. For the adsorption energy of A we use $\Delta g_A^A = 0 \text{eV}$.

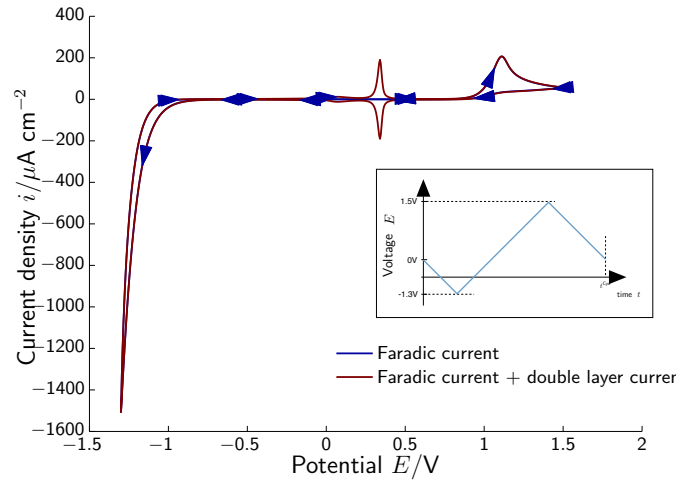
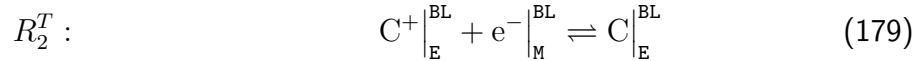
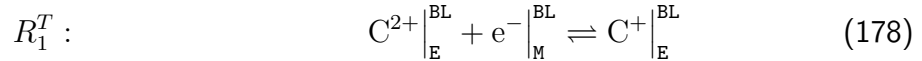


Figure 6: Numerical simulation of the cyclic voltammogram with double layer current and Faradaic current. Potential profile according to the subfigure.

This example shows that the faradaic current (peak at 1.2V) and the current due to the adsorption and discharge process $A^-|_E^{BL} - e^-|_M^{BL} - (\kappa_{A^-} - \kappa_A)H_2O \rightleftharpoons A_s$ (peak at 0.4 V) can be in the same order.

6.6.3 2-Step electron transfer

The final example is to consider a two step electron transfer reaction,



for which we consider a solution of A_2C with concentration 0.01M. Further, we consider bulk concentrations of for C^+ and C of 0.01M. The reaction parameters are

$$\Delta g_1^T = 0 \text{ eV} \quad i_1 = \{0.1, 1\} \quad (180)$$

$$\Delta g_2^T = -0.2 \text{ eV} \quad i_2 = \{0.1, 1\} . \quad (181)$$

We thus vary the exchange current density in this example.

Fig. 7 displays a numerical simulation of this example and the impact of the parameter variation of i_1 and i_2 .

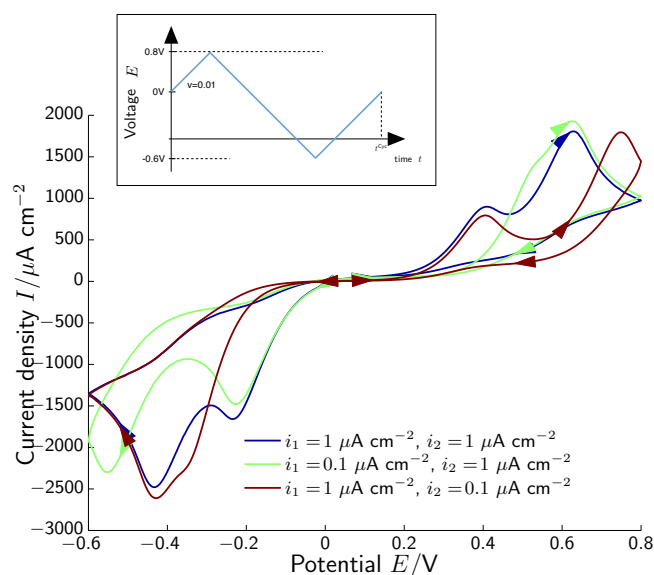


Figure 7: CV simulation of a 2-step electron transfer reaction-

6.7 Conclusion

We derived based on the framework of non-equilibrium thermodynamics the boundary conditions for a general electrochemical interface. The model was then applied to the metal-electrolyte interface based on some explicit material functions. Numerical simulations show the applicability of the model to double layer charging and transfer reactions. Extensive parameter studies will be performed in an upcoming publication. This approach can be considered as a first step towards a model based understanding of cyclic voltammetry.

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Appendix A Surface capacity

Here we provide a semi-explicit representation of the surface capacity C_s . First of all note that the surface charge q_s has the representation

$$q_s = - \frac{\sum_{\alpha=1}^{N_E} z_{\alpha} e_0 y_{\alpha} + \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} z_{\alpha} e_0 y_{\alpha,\beta}}{a_V^R y_V + \sum_{\alpha=0}^{N_E} a_{\alpha}^R y_{\alpha} + \sum_{\alpha=0}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} a_{\alpha,\beta}^R y_{\alpha,\beta}} . \quad (182)$$

With the representation y_{α} , $y_{\alpha,\beta}$ and y_V of [15] we obtain an expression of q_s in terms of $(\varphi - \varphi^E)$ and $(\gamma - \gamma^R)$, i.e. $q_s = \hat{q}_s(\varphi - \varphi^E, \gamma - \gamma^R)$. The surface charge is thus a function of φ_s and the surface tension γ . The surface fractions $y_{\alpha,\beta}$ obey the constraint

$$y_V(\gamma - \gamma^R) + \sum_{\alpha=0}^{N_E} y_{\alpha}(\varphi - \varphi^E, \gamma - \gamma^R) + \sum_{\alpha=0}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} y_{\alpha,\beta}(\varphi - \varphi^E, \gamma - \gamma^R) - 1 = 0 , \quad (183)$$

which is an implicit relationship between U_E and $\gamma - \gamma^R$. Hence, we may use the implicit function theorem to deduce a solution $\gamma = \hat{\gamma}(U_E)$ from equation (183), which satisfies $d\hat{\gamma}/d(U_E) = q_s$. The surface capacity C_s is thus

$$\hat{C}_s = \frac{d\hat{q}_s}{dU_E} = \left(\frac{\partial q_s}{\partial U_E} + q_s \cdot \frac{\partial q_s}{\partial(\gamma - \gamma^R)} \right). \quad (184)$$

With the (dimensionless) abbreviations

$$f_1 := \sum_{\alpha=1}^{N_E} z_{\alpha} y_{\alpha} + e_0 \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} z_{\alpha} y_{\alpha,\beta} \quad (185)$$

$$f_2 := y_V + \omega_0 y_0 + \sum_{\alpha=1}^{N_E} \omega_{\alpha} y_{\alpha} + \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} \omega_{\alpha,\beta} y_{\alpha,\beta} \quad (186)$$

$$f_3 = \sum_{\alpha=1}^{N_E} z_{\alpha}^2 y_{\alpha} + \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} z_{\alpha}^2 y_{\alpha,\beta} \quad (187)$$

$$f_4 = e_0 \sum_{\alpha=1}^{N_E} z_{\alpha} \omega_{\alpha} y_{\alpha} + e_0 \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} z_{\alpha} \omega_{\alpha,\beta} y_{\alpha,\beta} \quad (188)$$

$$f_5 = y_V + \omega_0 y_0 + \sum_{\alpha=1}^{N_E} \omega_{\alpha} y_{\alpha} + \sum_{\alpha=1}^{N_E} \sum_{\beta=-1}^{|z_{\alpha}|} \omega_{\alpha,\beta}^2 y_{\alpha,\beta} \quad (189)$$

we obtain for the surface capacity the expression

$$\hat{C}_s = -\frac{e_0^2}{k_B T a_V^R} \left(\frac{f_1 \cdot f_4 - f_3 \cdot f_2}{(f_2)^2} + \frac{f_1 f_4 \cdot f_2 - f_1 \cdot f_5}{f_2 \cdot (f_2)^2} \right). \quad (190)$$

Note that the term $\frac{e_0^2}{k_B T a_V^R}$ indeed has units $\frac{F}{m^2}$ and that all functions $f_k, k = 1, \dots, 5$, are dependent on U_E and $\gamma - \gamma^R$.

Appendix B Calculation of the Faradaic current

Reconsider that

$$r_{q_M}^{\text{Eff}} = r_{q_M}^{\text{Eff},'} + r_{s q_M}^{\text{Eff},r} \quad (191)$$

with

$$r_{q_M}^{\text{Eff},'} = e_0 \sum_{\alpha \in \mathcal{I}_M'} z_{\alpha} r_{\alpha}^{\text{Eff}} = -e_0 \sum_{\alpha \in \mathcal{I}_M'} z_{\alpha} \left(\sum_{\beta \in \mathcal{I}_E} \nu_{\beta,\alpha} R_{\beta}^T + \sum_{\beta \in \mathcal{I}_M^r} \nu_{\beta,\alpha} R_{\beta}^T \right) \quad (192)$$

$$r_{q_M}^{\text{Eff},r} = e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_{\alpha} r_{\alpha}^{\text{Eff}} = -e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_{\alpha} \left(\sum_{\beta \in \mathcal{I}_E} \nu_{\beta,\alpha} R_{\beta}^T + \sum_{\beta \in \mathcal{I}_M^r \setminus \{\alpha\}} \nu_{\beta,\alpha} R_{\beta}^T - R_{\alpha}^T \right) \quad (193)$$

We can thus rewrite

$$e_0 \sum_{\alpha \in \mathcal{I}_M'} z_{\alpha} R_{\alpha}^T - e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_{\alpha} \sum_{\beta \in \mathcal{I}_M^r \setminus \{\alpha\}} \nu_{\beta,\alpha} R_{\beta}^T - e_0 \sum_{\alpha \in \mathcal{I}_M'} z_{\alpha} \sum_{\beta \in \mathcal{I}_M^r} \nu_{\beta,\alpha} R_{\beta}^T \quad (194)$$

$$= e_0 \sum_{\alpha \in \mathcal{I}_M^r} \left(z_{\alpha} - \sum_{\beta \in \mathcal{I}_M \setminus \{\alpha\}} z_{\beta} \nu_{\alpha,\beta} \right) R_{\alpha}^T \quad (195)$$

Due to the electro-neutrality of each transfer reaction we have

$$z_\alpha - \sum_{\beta \in \mathcal{I}_M \setminus \{\alpha\}} z_\beta \nu_{\alpha,\beta} = \sum_{\beta \in \mathcal{I}_E} z_\beta \nu_{\alpha,\beta} \quad (196)$$

and obtain thus

$$r_{q_M}^{\text{Eff}} = e_0 \sum_{\alpha \in \mathcal{I}_M^r} z_\alpha^E R_\alpha^T - e_0 \sum_{\alpha \in \mathcal{I}_E^r} z_\alpha^M R_\alpha^T . \quad (197)$$